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ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 1

J. Carrell Morris, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

May 1964

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ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 1.

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(Continued on inside back cover.)

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ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 1.

by

J. Carrell Morris and Walter J. Weber, Jr.

for

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

A report submitted in fulfillment of a contract between the Public Health Service and Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts (Contract No. SAph 76295). Submitted May 15, 1962.

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service
Division of Water Supply and Pollution Control

May 1964

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, rural, where he lives, works, and plays; the air, water, and earth he uses and re-uses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

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Public Health Service Publication No. 999-WP-11

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems — problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne waste to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain — it must be the very lowest science and

engineering can achieve. Anything more will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

The authors of this report also collaborated on a previous report in this series (AWTR-2). In this first report they stated that ". . . the use of adsorbents and adsorptive processes is the most promising of currently known methods for the further treatment of secondary sewage effluents."

The present report describes the experimental program pursued for further investigation of the adsorption process. This report is the result of the first year's work on the project. Subsequent reports will be published giving detailed information on later work.

CONTENTS

	Page
Abstract	vii
Introduction	1
Research Objectives and Plan of Investigations	2
General Considerations	2
Selection and Preparation of Adsorbates	4
Sulfonated Alkylbenzenes	4
Phenol and Other Adsorbates	5
Stock Solutions of Adsorbates	6
Selection and Preparation of the Adsorbent	6
Sources of Adsorbents	6
Preliminary Treatment of Adsorbents	7
Selection of the Type of Carbon	7
Analytical Procedures	9
Experimental Methods	11
General Approach	11
Experimental Procedure	13
Rates of Adsorption	13
Observed Rates	13
Environmental Factors Affecting the Rate of Adsorption	17
Hydrogen Ion Concentration	17
Temperature	18
Kinetic Effects of the Nature and Concentration of Adsorbate	20
Concentration of Solute	20
Molecular Size of Substrate	22
Molecular Configuration of Substrate	25
Rates of Adsorption of Nitrochlorobenzenes and Octylphenoxyenneaethoxyethanol	28
Effects of Particle Size and Concentration of Carbon on Rates of Adsorption	28
Particle Size	28
Concentration of Carbon	30
Rates of Desorption	31

Page

Adsorption Equilibria 32
Reversibility 32
Adsorption Isotherms 34
Interpretation of Experimental Adsorption Isotherms . 41
Equilibrium Capacities and Adsorptive Tendencies . . 46
pH Effects 47
Effect of Temperature 48

Specific Surface Area 50

Competitive Adsorption 54
General Considerations 54
Rates of Adsorption 55
Capacities and Equilibria of Adsorption 59

Adsorbents Other Than Activated Carbon 62

Summary and Conclusions 64

Appendix A: Notations 71

References 73

ABSTRACT

Studies on the kinetics of adsorption on granular carbon showed that: (1) Uptake from dilute solution proceeds slowly for compounds of high molecular weight such as tetradecylbenzenesulfonate and dodecylbenzenesulfonate; equilibrium obtains only after several weeks. (2) The rate of adsorption is a linear function of the square root of concentration, that is, a greater fraction of solute is adsorbed per unit time the more dilute the solution, which implies that the process favors removal of trace quantities. (3) Rates of adsorption decrease considerably with increasing size of adsorbate when the amount adsorbed per unit time is expressed in molar units; when expressed in weight units the effect is much less pronounced. (4) The configuration of the adsorbate molecule affects rate of uptake: molecules with highly branched structures are removed much more slowly than those of identical molecular weight but with a configuration that permits coiling or attainment of compactness. (5) Rates of adsorption per unit weight of carbon vary reciprocally as the square of the diameter of individual carbon particles. (6) The rate of adsorption of alkylbenzenesulfonates increases with decreasing pH of the solution.

The findings correlate with equations derived for infraparticle diffusion, which indicates that the rate of adsorption is controlled by rate of diffusion of solute within the micropores of the carbon.

ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 1.

Introduction

A program of research on the adsorption of deleterious organic constituents of waste waters by selected granular adsorbents was initiated by the authors at Harvard University in May 1961, in accord with the terms of Contract No. SAph 76295 with the United States Public Health Service and in cooperation with the Advanced Waste Treatment Research Branch, Division of Water Supply and Pollution Control, Robert A. Taft Sanitary Engineering Center.

This report is a summary of work on adsorption performed in connection with the contract from May 15, 1961, through May 14, 1962. Research efforts during this first year have been primarily directed toward characterization of adsorptive phenomena in synthetic, experimental systems of selected biochemically resistant organic compounds and granular adsorbents, with prinicpal emphasis placed upon activated carbon as the adsorbent because of its proven adsorptive capacity and its promise for practical application in waste-water treatment. Because it is anticipated that practical applications of adsorption in waste-water treatment will entail columnar operation, and because such processes are most feasibly executed with a granular material, the research has been conducted with this form of adsorbent.

The solutes that have been investigated are typical of biochemically resistant materials often found in conventionally treated waste-water effluents and in receiving waters into which such effluents are discharged. These include anionic synthetic detergents, alkylbenzenesulfonates (hereafter referred to as ABS when used in a general sense), a nonionic synthetic detergent (Triton X-100), and nitrochlorobenzene. Of the persistent organic compounds certain alkylbenzenesulfonates currently occur frequently and are troublesome. Consequently, much of the research has been devoted to an extensive examination of the adsorption of these materials on activated carbon.

The studies on adsorption have included investigations of rates at which the process occurs under varying conditions of adsorbate, adsorbent, and systemic environment; of adsorptive

equilibria under similarly varied conditions; and of the ultimate capacities of the experimental adsorbents for adsorption of these selected materials.

This is primarily a report of research progress rather than a complete description of how adsorption may be used to optimum advantage in waste-water treatment practice, and as such provides only a summary of experimental observations and findings to date. Extension of this research, currently underway, should provide supplementary information that will, along with the data presented herein, be of considerable use in the final design of appropriate adsorption processes. Portions of this report have been reprinted in part from previous publications by the authors on their studies of adsorption under Contract SAph 76295 (see references 14, 15, and 16); the present report brings together the results of these studies and also describes research results previously unpublished.

RESEARCH OBJECTIVES AND PLAN OF INVESTIGATIONS

General Considerations

Development of a practical, economical method of removal of persistent organic contaminants from waste waters is essential for conservation of the quality of water resources, for reduction of costs of treatment of previously polluted water supplies, and for provision of potential additional re-use of water in areas where supplies are limited. Since current methods of treatment of waste waters can economically and effectively remove a large percentage of suspended matter and those materials prone to biochemical oxidation, major consideration need be given only to materials inefficiently removed by present techniques, of which ABS is a prime example. The process for this type of renovation of waste water may thus be considered, at least for the present, as a "third-stage" or "tertiary" treatment to be imposed on effluents from conventional secondary-treatment plants.

Although ABS, currently the most noticeably offensive material, has been used to date as the focal point of these studies, a generally feasible method should have great breadth of application. If any method is to be widely applicable to the further purification of waste waters it must be capable of removing a great variety of organic materials. Moreover, it may be anticipated that the nature and individual concentrations of the offensive organic materials will not be known fully.

The first stage of conventional waste-water treatment is primarily a physical process of screening and sedimentation, while the second stage is biological. Unless complete phase separation is used, as in distillation or freezing, some form of chemical treatment seems indicated for the proposed third stage. It should of course be economical and relatively easy to operate.

The types of operation that now appear to meet to some extent these minimum requirements are adsorption and foam fractionation. Adsorption has the advantage of applicability to the removal of a wide variety of organic compounds. The forces of adsorption are generalized and primarily physical; consequently, adsorption is not limited to nearly the same extent by the chemical structures of the organic contaminants as are many other methods. For example, direct foam fractionation requires that the contaminant be surface active; chemical oxidation depends upon susceptibility to oxidation; and efficient coagulation with aluminum sulfate apparently calls for an ability to form chemical bonds with aluminum.

Adsorption on activated carbon has long been recognized as one of the basic unit operations for the purification of solutions; its use is often indicated when the removal of contaminants from solution cannot be accomplished efficiently or economically by other conventional physical or chemical processes such as filtration or precipitation. Activated-carbon treatment of liquid media is a relatively simple operation requiring a minimal physical plant and no elaborate specialized equipment.

Of prospective processes for the renovation of waste water, adsorption on carbon is probably most nearly related to present methods of treatment of water supplies. Activated carbon is already widely used for reduction of tastes and odors, and the success of the carbon filter for isolation of a wide range of pollutants from water has shown that activated carbon is an effective absorbent for many materials.

Nonetheless, current general practice in the use of activated carbon for improvement of the organoleptic quality of water appears unsuitable for large-scale renovation of waste water. Mixing of powdered carbon with water for a limited time, followed by filtration and rejection of the carbon, is a costly and relatively inefficient use of the absorbent. For example, a carbon would be rated as effective with a phenol value of 20, which corresponds to adsorption by carbon of 10 micrograms of organic material per 20 milligrams of carbon or

0.45 percent. As will be shown later, adsorptive capacities of at least 10 percent should be realizable with full use of the carbon.

Best use of carbon or other adsorbents will probably be attained by columnar, countercurrent operation in which the entering, highly polluted water comes into contact with nearly exhausted adsorbent and, as it becomes purified, encounters fresher and fresher adsorbent until at the exit of the column it receives a final polishing with fully active material.

This process would appear to be most feasibly executed with the adsorbent in granular form. Accordingly, the experiments to be described have been performed with this form of material to ascertain its adsorptive characteristics and determine conditions for its use.

Of the known organic contaminants of concern, ABS presents some of the most widespread problems in both waste and receiving waters. Efficient removal of these surfactants is a primary function that any method of waste-water renovation must fulfill; its ability to do so determines to a large extent its immediate applicability to advanced waste treatment.

Accordingly, an extensive program of research on the adsorption of ABS and other resistant materials on granular activated carbon has been undertaken to gain a more complete understanding of rates of adsorption, adsorptive capacities, and equilibria of adsorption in these systems, and to evaluate in detail the prospective worth of adsorption on carbon as a method of removing surfactants and similar compounds from waste waters.

SELECTION AND PREPARATION OF ADSORBATES

Sulfonated Alkylbenzenes

Since fundamental information pertinent to the interpretation of adsorptive characteristics in ABS-carbon systems was desired, the experiments had to be conducted with well-defined materials. Technical-grade ABS is composed of mixtures of isomers and homologues resulting from the polymerization of olefins such as propylene, and from the alkylation of benzene with the polymerized olefin. Consequently, these technical products contain a number of compounds of different molecular size and structure. Furthermore, during the usual process of manufacture of the detergents, excess sulfuric acid used in sulfonating the alkylbenzene is neutralized and appears as sodium sulfate in the technical product.

Such material seemed clearly unsuited for quantitative studies of adsorptive mechanism, so materials of much greater purity were sought. Moreover, to evaluate the effects of size and structure of the alkyl group on adsorption, pure homologues of known structure were required.

Materials of the needed purity and structure are not, however, commercially available, and synthesizing them would have been extremely laborious, time consuming, and expensive. Fortunately, small quantities of many of the desired pure compounds were found to have been prepared by the Research and Development Department of the Continental Oil Company, Ponca City, Oklahoma, in connection with one of their own research projects. This group kindly consented to provide 2 grams each of the (2-hexyl)-, (2-octyl)-, (2-decyl)-, (2-dodecyl)-, (3-dodecyl)-, (6-dodecyl)-, and (2-tetradecyl)benzenesulfonates as their sodium salts. The materials were specified as being 98 to 99 percent pure in terms of the structure of the alkyl group and the location of the benzene ring. There was no attempt to separate isomers formed during sulfonation, so that, though the sulfonate group was primarily in the para position, some of the other isomers were undoubtedly present.

In addition to the pure compounds, a typical technical-grade sodium dodecylbenzenesulfonate was obtained from the Petrochemical Department of the Continental Oil Company. This material was used to provide a comparison of the adsorptive properties of a typical commercial surfactant with those of the pure sulfonated alkylbenzenes. An analysis of this material showed 92.9 percent active material plus 6.8 percent sodium sulfate, 0.4 percent moisture, and no measurable amount of free oils. The active material consisted of branched and straight-chain molecules with an average molecular weight equal to that of dodecylbenzenesulfonate.

Phenol and Other Adsorbates

The characteristics of the adsorption of phenol on activated carbon are known better than those of the adsorption of ABS. Considerable work has been done with the phenol-carbon system and, indeed, phenol has often been used as a reference material for estimating surface areas of carbon preparations. Consequently, studies on this system were deemed desirable to serve as a bridge between this research and the work of others. Phenol was also used as a reference compound, the specific surface area of carbon being determined on the basis of its capacity for mono-layer adsorption of phenol. The chemical was obtained as a standard solution containing 1.000

gram of phenol per liter from Howe and French, Inc., Boston, Massachusetts.

Other adsorbates used were sodium benzenesulfonate, sodium p-toluene-sulfonate, ortho- and para-nitrochlorobenzenes, sodium dodecyl sulfate, and octylphenoxyenneaethoxyethanol (Triton X-100). The former four materials were obtained as reagent-grade products from Eastman Organic Chemicals; the sodium dodecyl sulfate, a Matheson, Coleman, and Bell product, was better than 95 percent pure in dodecyl sulfate and 99.5 percent pure in total alkyl sulfate by analysis; Triton X-100 was obtained as a 99 percent minimum-active-ingredient solution from the Rohm and Haas Company.

Stock Solutions of Adsorbates

To eliminate from the experimental system all extraneous materials that might have introduced sources of error or interference, all stock solutions and solution phases of the experimental systems were prepared with twice-distilled water. Cambridge tap water was first distilled in a conventional tin-lined still, and the condensate was transferred into an all-glass still for redistillation. Preliminary boiling with escape of steam was used to purge the water of dissolved $C0_2$ and $C1_2$ prior to collection of the condensate from the redistillation.

Stock or working solutions of all the adsorbates except the phenol were prepared at a standard concentration of 10^{-4} molar by weighing appropriate quantities of the chemicals and dissolving them in suitable volumes of the glass-distilled water. The phenol was merely diluted to 10^{-4} molar with glass-distilled water to obtain a stock solution.

SELECTION AND PREPARATION OF THE ADSORBENT

Sources of Adsorbents

A number of activated carbons were studied during the preliminary, exploratory phase of the research. The carbons tested were all commercially available, preactivated materials procured directly from their respective manufacturers. Numerous samples of materials were obtained from: West Virginia Pulp and Paper Co. (Nuchar C-190); American Norit Co. (Norit); National Carbon Co. (Columbia LC); Fisher Chemical Co. (Fisher); and Atlas Powder Co. (Darco S-51).

These carbons were manufactured from a variety of raw materials. Nuchar C-190 is derived from a "black-ash"

byproduct of a chemical pulping process. Norit carbon is manufactured from wood charcoal; Darco from lignite; Columbia and Fisher from cocoanut shell.

Preliminary Treatment of Adsorbents

The granular adsorbents received from the manufacturers were subjected to additional size fractionation and cleaning, prior to being comparatively tested in preliminary studies to assess their relative merit for intensive experimentation on adsorption.

Each of the materials was first crushed and then separated, by sieving, into uniform particle sizes. From these, two sizes were chosen for most studies: 50/60, that is, particles that pass a U.S. Standard Sieve number 50 but not a number 60; and 100/140, that is, particles that pass a number 100 sieve but not a number 140. Arithmetic mean diameters for the two groups of particles were 0.273 and 0.126 millimeters respectively.

After separation, the sized samples of carbon were washed three times in double-distilled water to remove any dust remaining from the crushing process, then dried in thin layers at 105°C for 24 hours.

Selection of the Type of Carbon

Criteria for selection of the particular carbon to be used for the main experimental work were high adsorptive capacity, freedom from materials that might interfere with analytical methods, ease of preparation in desired particle sizes, and resistance to attrition.

Included in the assessment of adsorptive capacity was a consideration of adsorptive rates, with the evaluation of a characteristic rate constant based upon adsorption of sodium(2-dodecyl)benzenesulfonate from aqueous solution. The activated carbons tested were found not to vary appreciably in rates of uptake of the sulfonated alkylbenzene. Figure 1 illustrates the respective rates of removal of the solute from solution by the different carbons.

The equilibrium adsorptive "capacities" of the several adsorbents were evaluated from the specific amounts of benzenesulfonate and (2-dodecyl) benzenesulfonate adsorbed from dilute aqueous solutions of these materials. Table 1 lists the measured adsorptive capabilities of the several materials

and further illustrates the similarity of the various carbons in this regard. The values given in Table 1 are not true capacities, but are equal to the mean values of x/m over a range of concentrations of solute (10μmol/liter to 30μmol/liter) corresponding to the plateaus of the respective adsorption isotherms.

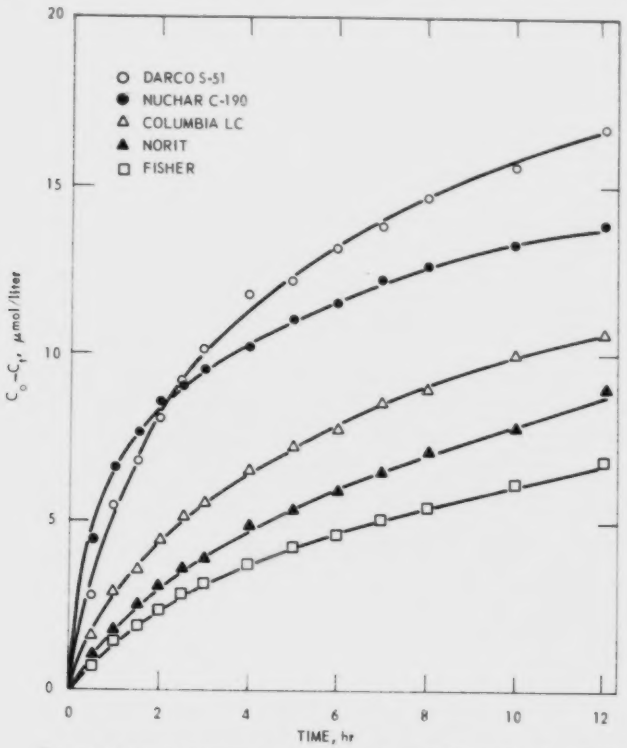

Figure 1. Rates of adsorption for selected carbons (30°C, 75.0 mg/liter 0.273 mm activated carbon, [2-dodecyl] benzenesulfonate, C_o = 29 μmol/liter).

Table 1. ADSORPTIVE CAPACITIES OF ACTIVATED CARBONS (30°C, 0.273 mm PARTICLE SIZE)

Carbon	Uptake of benzene-sulfonate, μmol/g	Uptake of (2-dodecyl) benzenesulfonate, μmol/g
Columbia LC	131	400
Darco S-51	101	420
Fisher	120	344
Norit	92	338
Nuchar C-190	54	316

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Since analyses of the experimental solutions were based on measurements of ultraviolet absorbance, it was important that the carbon used be free from leachable impurities exhibiting light absorption in the ultraviolet region. Accordingly suitable quantities of each of the carbons studied were subjected to extractive treatment for 5 hours in a Soxhlet apparatus and then the absorption spectra of the extracts were measured. Both benzene-methanol and distilled water were used as extractants.

Benzene-methanol extracts of the Fisher and Darco carbons exhibited appreciable absorption in the ultraviolet region and so were discarded as potential adsorbents. The distilled water extracts from the Nuchar C-190 and Norit also showed strong absorption at wave lengths shorter than 240 millimicrons. On the other hand the absorbance of extracts from the Columbia LC Carbon differed from that of pure water only slightly over the entire range from 340 to 220 millimicrons.

In addition the Columbia LC Carbon was a relatively hard, abrasive-resistant material in comparison with others like the Nuchar C-190, which disintegrated or abraded significantly in batch studies.

Accordingly, since it met all the preliminary criteria, Columbia LC Carbon was chosen as the adsorbent to be used in these studies of the adsorption of ABS on activated carbon.

It was noted that the water extract from the Columbia LC Carbon was acidic, whereas those from the Nuchar C-190 and Norit were basic. The pH value of the extract from Columbia LC Carbon was 5.18, from Nuchar, 9.60, and from Norit, 9.56 as compared with an average pH of about 6 for the distilled water. The significance of this factor with regard to effectiveness of adsorption from aqueous solutions is not known. Presumably it indicates differences in method of preparation and activation of the individual carbons and also reflects differences in the character of the adsorptive surfaces.

ANALYTICAL PROCEDURES

Rapid determinations of the concentration of solute in the pure solutions was possible because all the materials studied, except sodium lauryl sulfate, exhibit intense, characteristic adsorption of ultraviolet radiation. Accordingly, ultraviolet spectrophotometry was employed for the analytical determinations.

Difficulty was encountered in making quantitative measurements because of strong adsorption of ABS on the quartz surfaces of the adsorption cells. After considerable experimentation with various techniques, it was found that the adsorption was decreased to a satisfactory extent in the presence of potassium dihydrogen phosphate.

Accordingly all glassware and quartz ware used for the analytical determinations was prerinsed with phosphate solution and all measurements of absorbance were made in 0.01 molar phosphate solution. The items were first cleaned with acid-dicromate solution and rinsed with hot water, then were washed with 1 molar HCl and again rinsed with hot water, and finally were rinsed several times with glass-distilled water, followed by a rinse with 0.01 molar phosphate solution. Reaction vessels, storage bottles, and other glassware were cleaned similarly, but the final rinse with phosphate was omitted.

Standard solutions of the adsorbates were prepared for calibration by dissolving accurately weighed quantities of the desiccated materials in 0.01 molar phosphate to make 10^{-4} molar solutions. Appropriate dilutions of these solutions were made with 0.01 molar phosphate to give series of solutions suitable for spectrophotometric calibration.

For the range of concentrations studied, all the solutions conformed excellently to the Beer-Lambert Law, showing good proportionality of absorbance to concentration at the wavelengths used. The long-chain alkylbenzenesulfonates and the octylphenoxyenneaethoxyethanol each showed an absorption maximum at 225 millimicrons. A similar absorption maximum for p-toluenesulfonate occurred at 220 millimicrons. Benzenesulfonate did not show an absorption maximum in this region; a plateau of high absorption was, however, observed at short wavelengths, and measurements were made at 215 millimicrons. Phenol exhibited an absorption peak at 271 millimicrons, orthonitrochlorobenzene at 260, and paranitrochlorobenzene at 280.

The procedure for analysis was to pipet a 10.0-milliliter sample from the solution in the reaction vessel and introduce this into 10.0 milliliters of 0.02 molar phosphate. The mixed solution was then placed in a 5-centimeter quartz cell, and its absorbance at the appropriate wavelength was measured against a 0.01 molar phosphate solution as blank by means of a Beckman spectrophotometer, model DU. The concentration was then computed from the appropriate value of absorptivity. Reproducibility of results was 1 to 2 percent except for very low concentrations.

This rapid and simple method cannot be used for waste waters containing numerous solutes, for marked interference by

other materials occurs. When polluted or waste water was being studied, recourse was had to the Longwell and Manjece modification of the Jones method of using methylene blue. [1] Since this method is tedious and less precise than the one previously described, experimental data were much more limited when it had to be used.

Determinations of phenol in concentrated solutions used for evaluation of total surface area were made by formation of tribromophenol with an excess of standard bromine and by measurement of the quantity of bromine consumed in the reaction. The standard bromine was generated from a bromate-bromide mixture with acid, and the excess was determined by reaction with iodide followed by titration with standard thiosulfate. [2]

EXPERIMENTAL METHODS

General Approach

Two types of experimental procedure were considered for use in the portion of the research dealing with kinetics of adsorption: A column arrangement in which the adsorbate solution would be percolated through a bed of the adsorbent with samples taken periodically from the effluent; and a batch operation in which the carbon and the adsorbate solution would be continuously shaken together, with samples withdrawn periodically from the reaction vessel.

The batch technique was selected because of its relative simplicity. Advantages of the technique that figured significantly in its selection were freedom from complex hydraulic parameters indigenous to flow-through systems, adaptability to small-volume work, ease of investigation of variations in conditions, and general facility of operation.

Although final technical systems will probably utilize column-type operation, the evaluation of the fundamental characteristics of adsorption is simpler with a batch technique. If suitable functional relationships are established for the variables, extrapolation of data from closed systems for the prediction of behavior in continuous systems is possible.

The techniques employed for equilibrium studies differed only slightly from those used in the investigation of reaction kinetics. In the latter case the reaction vessels were 4,000-milliliter Pyrex-glass bottles, in which solutions were agitated with Teflon-coated stirring rods, extending directly into the

adsorbate solution and connected to synchronous motors operating at 1,550 rpm. Preliminary kinetic studies had shown, as indicated in Figure 2, that the rate of adsorption was independent of stirring rate at rotations greater than a few hundred rpm. Temperature control for the rate studies was maintained by immersing the reaction vessels in water baths, thermoregulated to 0.1°C.

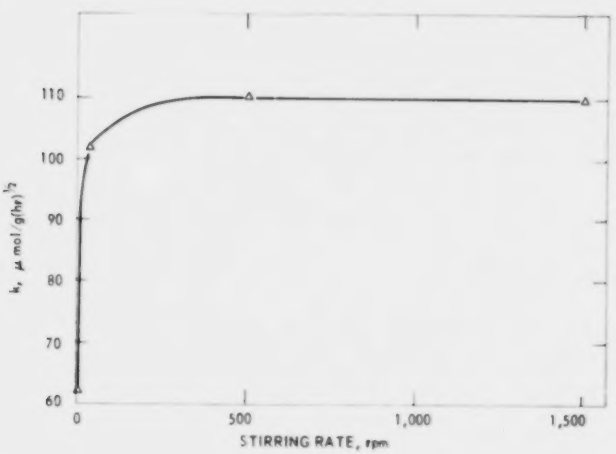

Figure 2. Variation in rate of adsorption with rate of stirring (25°C, 35.0 mg/liter, 100/140, 0.126 mm Columbia Carbon, [3-dodecyl] benzenesulfonate).

The reaction vessels used in the equilibrium investigations were much smaller, 300 milliliters, and agitation was provided for in most cases by placing the flasks in conventional laboratory shakers. A special shaking apparatus with a capacity for a great number of reaction vessels was used at one stage when more than 200 reaction flasks had to be shaken simultaneously. Two conventional, oscillating laboratory shakers were placed on a rectangular rack mounted on rollers, which had been fastened at each corner with a slack tie rope. When the shakers were operated out of phase with one another, effective agitation was provided for all the reaction vessels on the rack. Investigations on adsorption equilibria were made in rooms of reasonably uniform temperature, so that fluctuations in the temperatures of the solutions were no more than 2°C during a study.

Experimental Procedure

For each experiment on rate of adsorption an exact 3-liter volume of solution of adsorbate was prepared by diluting a sufficient volume of a 10^{-4} molar stock solution to give the desired concentration; this was done directly in a 4-liter reaction vessel. The reaction vessel containing the solution of adsorbate was then placed in a water bath for approximately 24 hours to allow the solution to attain the desired temperature and reach adsorptive equilibrium with the surfaces of the vessel. Prior to introduction of a suitable, accurately weighed amount of carbon into the vessel, an initial sample of 10 milliliters was removed and analyzed for concentration of adsorbate. This gave an accurate check on the preparation of the solution, and of course served as the reference concentration for the rate study. The carbon was then introduced into the vessel and rapidly dispersed by the motor-driven stirrer operating at 1,550 rpm. At appropriate intervals the stirring was briefly interrupted while 10-milliliter samples of the supernatant solution were pipetted from the reaction vessel; the samples for analysis resulted in some small decrease in total adsorbate available to the adsorbent, but each sample was only 0.3 percent of the total volume and the cumulative error of 2 to 3 percent was not significant for this type of experiment.

Preliminary kinetic studies had indicated that completion of the adsorption of ABS on granular activated carbon was attained only after periods of 2 to 3 weeks. A modified technique was, therefore, used for the investigation of adsorptive capacities and equilibria. A large volume of adsorbate solution was prepared as before, and 250-milliliter portions of this solution were dispensed into 300-milliliter glass-stoppered bottles. A suitable, accurately weighed amount of adsorbent was then added to each bottle, the weights being varied to cover the range of interest, except that two bottles were left without carbon for use as blanks. The bottles were then tightly stoppered and placed in an oscillating shaker to be shaken for 1 to 3 weeks, the longer time being used for all the surface-active sulfonates. Samples of all the solutions were analyzed at the end of the appropriate period; the amounts of adsorption were computed from the differences among the concentrations of adsorbate measured for the blanks and for the reacted solutions.

RATES OF ADSORPTION

Observed Rates

Preliminary investigations on rates of adsorption from solutions of ABS at concentrations comparable to those encountered in waste waters indicated that the adsorption proceeds

much more slowly than was anticipated. In Figure 3 is shown a plot of typical data on the adsorption of (2-dodecyl)benzenesulfonate by granular Columbia LC Carbon as a function of time. Adsorption is indicated by the decreasing concentration of solute remaining in solution. It is evident that the relatively rapid initial rate of adsorption decreases markedly within an hour or so to give a very gradual approach to an equilibrium condition, which is attained completely only after many days of contact between solution and carbon. The ultimate uptake of solute by the carbon under the experimental conditions applying to the data of Figure 3 is equivalent to approximately 27 micromoles per liter; thus only about 2 micromoles of ABS per liter are left finally in solution. After 12 hours only about 40 percent of the final uptake has occurred and yet the rate of adsorption has decreased to approximately one-sixth of the initial rate.

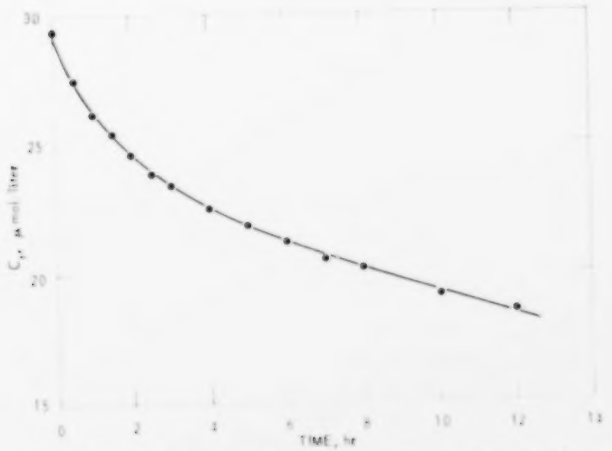

Figure 3. Rate of uptake of (2-dodecyl)benzenesulfonate by Columbia Carbon (30°C, 75.0 mg liter, 0.273 mm Columbia Carbon, C_t = concentration of solute remaining in solution at time t).

In Figure 4 data from some typical, long-term, kinetic studies carried out for over 200 hours are shown. While quantitative interpretations of the data of Figure 4 cannot be as significant as those of Figure 3, owing to the error introduced by volume depletion during the long-term studies, the plot illustrates the abrupt decrease in rate as the adsorption proceeds and the slow approach to final equilibrium.

The rate pattern illustrated in Figures 3 and 4 can be most readily accounted for if it is supposed that the rate of adsorption is controlled by the rate of diffusion of solutes in the internal capillary pores of the carbon particles. This type of mechanism has previously been postulated as a rate-controlling step in the uptake of other solutes by different types of granular adsorbents, including carbon. [3]

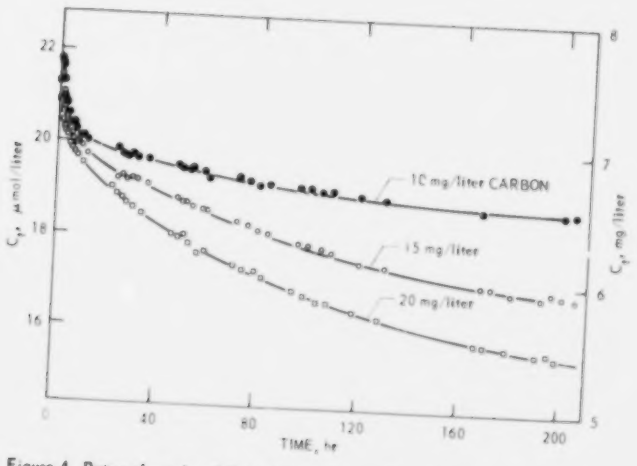

Figure 4. Rates of uptake of (3-dodecyl)benzenesulfonate by Columbia Carbon (30°C, 0.273 mm Columbia Carbon, C_t concentration of solute remaining in solution at time t).

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships, which differ in form as a function of the geometry of the adsorbent particle. [4] While mathematical treatment of the diffusion process will not be presented, one characteristic of the theoretical expressions will be described to facilitate presentation of the data. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half-power of time, $t^{1/2}$, rather than with t; nearly linear variation of the amount adsorbed with $t^{1/2}$ is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Such a variation was found in the present studies as shown by Figure 5 in which two of the sets of data in Figure 4 have been replotted on a $t^{1/2}$ scale. Good linearization of the data is observed for the initial phase of the reaction in accordance with

expected behavior if intraparticle diffusion is the rate-limiting step. Similar linearization was observed for all the other experiments with ABS and selected organic adsorbates.

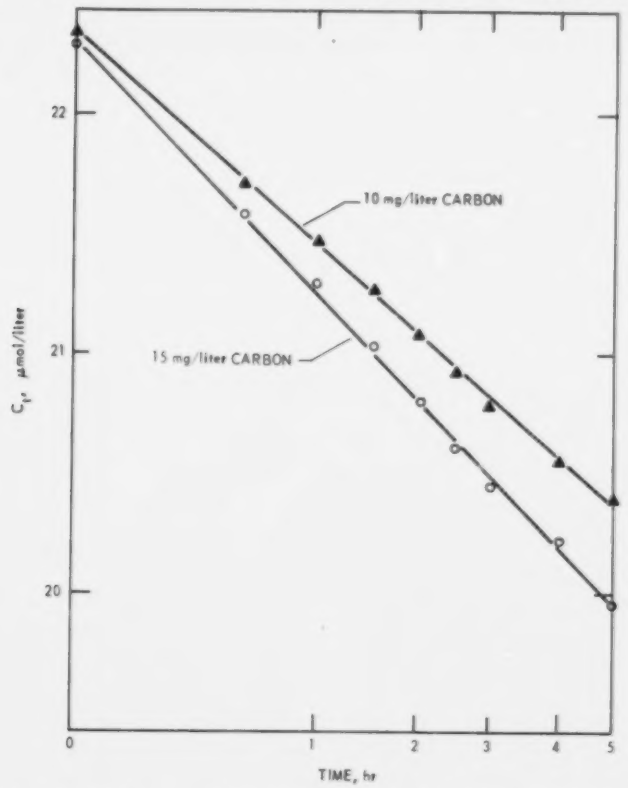

Figure 5. Plot of concentration vs time for diffusion ([3-dodecyl] benzenesulfonate, 30°C, 0.273 mm Columbia Carbon).

This linearization greatly aids comparison among relative rates of adsorption, and this comparison will be made later with the constant initial slopes obtained from $t^{1/2}$ plots. Although the k values thus obtained do not have usual dimensions for rate constants and cannot strictly be so termed, relative values for approximately similar conditions should be significant as rate parameters. The k values used have a dimension of $t^{-1/2}$ and are expressed in units of solute molarity per weight of carbon-square root of time, [e.g., k = mmol/g(hr) $^{1/2}$] .

ENVIRONMENTAL FACTORS AFFECTING THE RATE OF ADSORPTION

Hydrogen Ion Concentration

Figure 6 shows the effect of solution pH on the observed rate of uptake of (3-dodecyl)benzenesulfonate by Columbia Carbon. The increase in rate observed for decreasing pH may be attributable to alterations, particularly electrokinetic, in the carbon surface with changing hydrogen ion concentration. A decrease in pH probably results in a reduction of the negative charges at the surface of the carbon, which enhances the adsorption of the negatively charged alkylbenzenesulfonates.

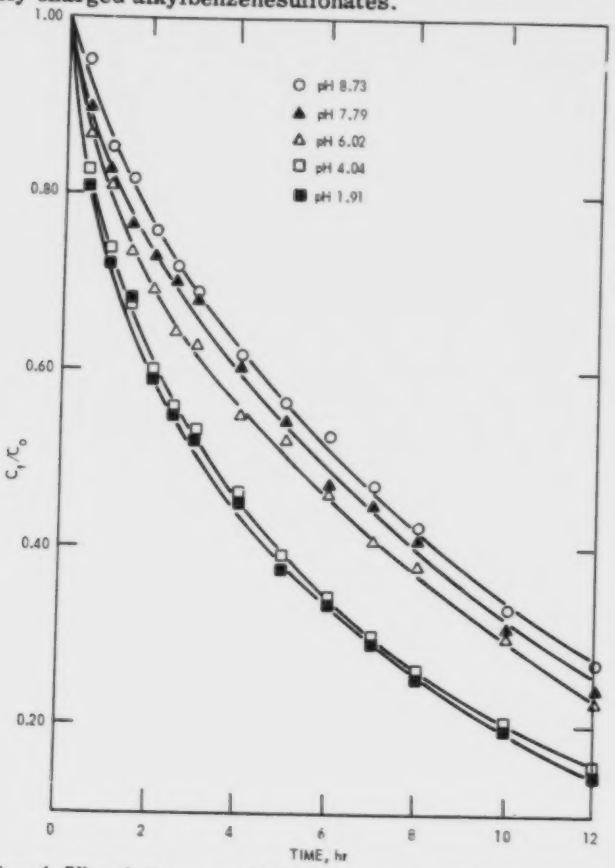

Figure 6. Effect of pH on uptake of ABS by Columbia Carbon (30°C, C_o = 14.4 μM [3-dodecyl] benzenesulfonate, 35.0 mg/liter, 0.126 mm Columbia Carbon).

Temperature

Further evidence that the rate of uptake of ABS by granular activated carbon in these studies was controlled by intraparticle diffusion is afforded by the temperature dependence of the rate of adsorption. Figure 7 shows the results of a series of kinetic experiments at six different temperatures between 5 and 55°C.

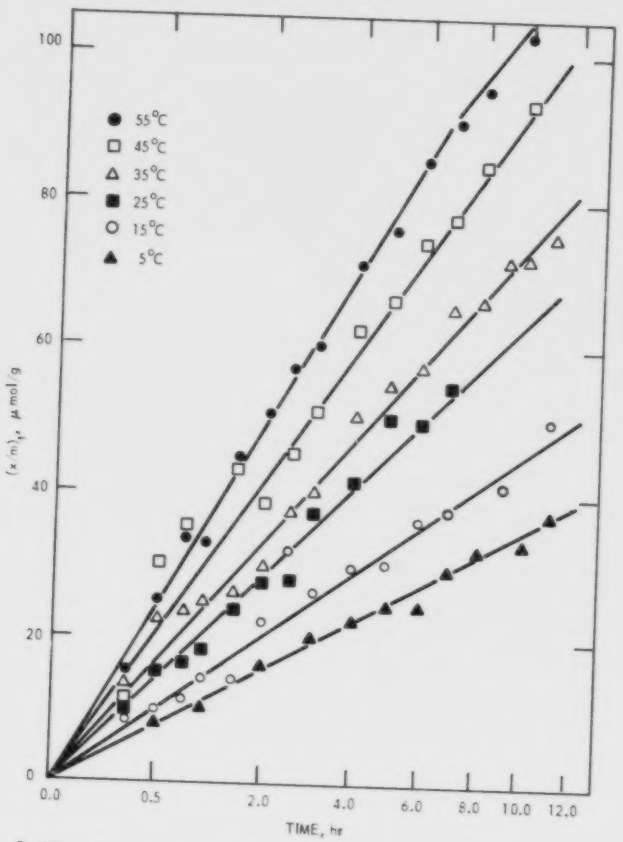

Figure 7. Effect of temperature on rate of adsorption (Na [3-dodecyl] benzenesulfonate, 100.0 mg/liter, 0.495 mm Columbia Carbon).

The increase in rates of reaction with increasing temperature is described by the equation

$$k = Ae^{-E/RT} \quad (1)$$

in which k is the specific rate constant, A is a temperature-independent factor sometimes called the frequency factor, and E is the activation energy, representing the minimum energy the reacting system must have for reaction to occur. Within moderate temperature ranges the values of the quantities A and E may be considered to remain constant.

Equation (1) may be written in logarithmic form as

$$\ln k = \ln A - \frac{E}{RT} \qquad (2)$$

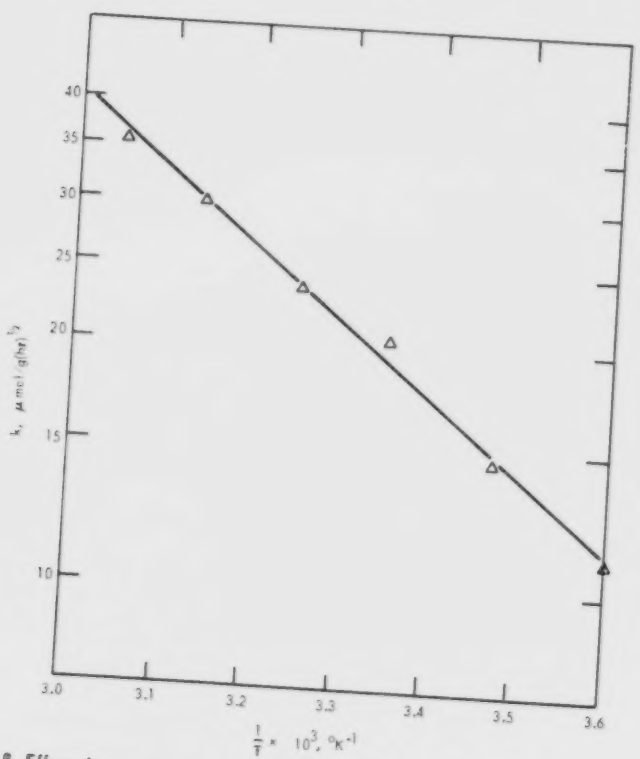

Figure 8. Effect of temperature on rate of adsorption (3-dodecyl benzenesulfonate, 100 mg/liter, 0.495 mm Columbia Carbon).

so that a linear relation should occur between ln k and 1/T. In Figure 8, k values, determined from the slopes of the linear plots of Figure 7, have been plotted logarithmically as a function of the

reciprocal of the Kelvin temperature. According to Equation (2), the slope of the straight line fitting the points of Figure 8 is $-\frac{E}{2.303R}$. Equation (2) may be written for any two rates, k_1 and k_2, and the difference expressed as

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E(T_1 - T_2)}{RT_1T_2} \qquad (3)$$

where R is equal to 1.986 calories per mole. Then, by considering any two temperatures lying within the experimental range, say 322.58 and 277.78°K, the corresponding rate values from Figure 8 are 33.0 and 11.3 micromoles per gram (hour) $^{1/2}$ respectively. Hence, $k_1/k_2 = 2.93$, $\ln k_1/k_2 = 1.08$, $(T_1T_2)^{-1} = 11.16 \times 10^{-6}$, and $(T_1-T_2) = 44.80$. The experimental activation energy is then calculated to have the value

$$E = \frac{(1.08)\,(1.986)\,(10^6)}{(4.480)\,(11.16)} = 4.27 \text{ kcal/mol}$$

Variations of diffusion rates with temperature for large molecules similar in size to the sulfonated alkylbenzenes have been found to conform to apparent activation energies of 3 to 5 kilogram-calories per mole, or slightly greater than that for the increase in fluidity or water with temperature.[5] It is apparent that the value, 4.3 kilogram-calories per mole, lies within the expected range for diffusion-controlled processes.

KINETIC EFFECTS OF THE NATURE AND CONCENTRATION OF ADSORBATE

Concentration of Solute

Prediction of the variation of rate of adsorption of ABS on carbon as a function of solute concentration is difficult. If the mechanism is as already outlined: rapid formation of an equilibrium interfacial concentration followed by slow diffusion into the carbon particles, then a simple dependence is not to be expected. Moreover, the mathematical treatment of intraparticle diffusion does not lead to a simple algebraic relationship between external solute concentration and time of reaction even when a constant saturated external layer is maintained.

Accordingly correlation has been made empirically of initial k values, obtained from plots of C_t against $t^{1/2}$, as a function of initial concentration of adsorbate.

The data in Figure 9 demonstrate that rates of absorption increase with increasing concentration of solute. The variation is not a linear one, however; as Table 2 shows, it is the ratio of k values to square root of concentration that is constant for these

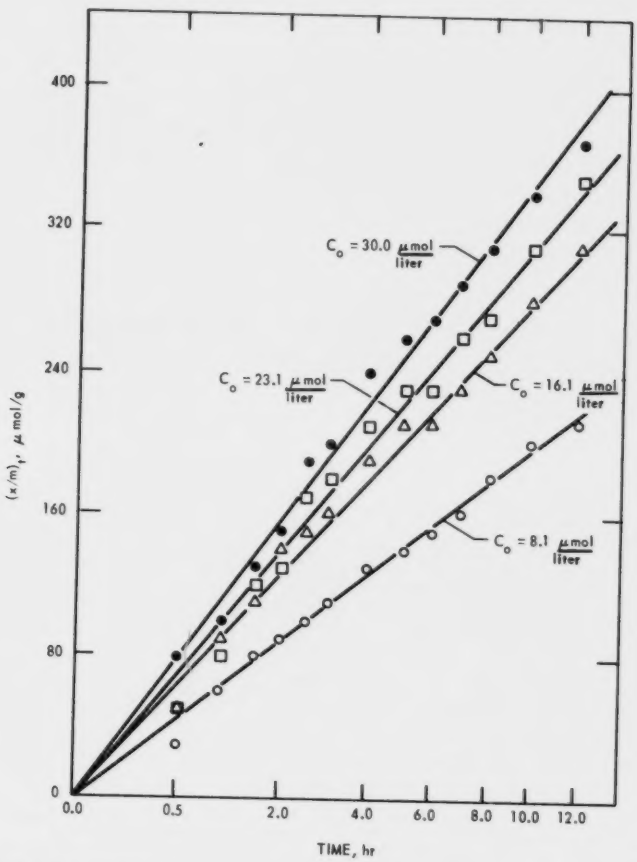

Figure 9. Effect of initial concentration of solute on rate of adsorption (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon, [3-dodecyl] benzenesulfonate).

data. The ratios of k values squared to initial concentration would, of course, have a similar constancy, and this ratio has the advantage of a first-order time dependence.

This form of concentration dependence should not be taken as universal, for theoretical equations for intraparticle diffusion indicate that it will vary depending on the characteristics of the adsorption isotherm and the fraction of the solute adsorbed at equilibrium. It is considered for the present to be just a useful relationship for correlation of data within the range of experimentation.

To the extent that this relation is valid, adsorption of ABS from water is relatively more rapid the more dilute the solution, that is, a greater fraction of solute will be adsorbed in a given period of time. This is advantageous for the removal of final traces of material in the renovation of a waste water.

Table 2. EFFECT OF INITIAL CONCENTRATION OF SOLUTE ON RATE OF ADSORPTION ([3-DODECYL] BENZENE-SULFONATE, 35.0 mg/liter, 0.126 mm COLUMBIA LC CARBON, 30°C)

C_o, μmol/liter	k, μmol/g(hr)$^{1/2}$	$k/C_o^{1/2}$
8.1	62	21.8
16.1	88	21.9
23.1	99	20.6
30.0	112	20.4

Molecular Size of Substrate

If diffusion of solute molecules within the micropore structure of activated carbon is considered to be the rate-determining step in the adsorption of ABS, then the size of the diffusing molecule should affect the overall rate of adsorption. The larger the molecule, the lower should be the rate at which it diffuses and hence the lower the rate of adsorption.

Figure 10 illustrates the dependence of rate of uptake on the length of the aliphatic hydrocarbon chain of the solute for a series of homologous (2-alkyl)benzenesulfonates. Moreover, the uptake curve for phenol, which serves as a control in the sense that the intraparticle diffusion of this molecule has been previously studied, [3] is shown in Figure 11 along with plots for two simple aromatic sulfonates having molecular weights smaller than those of the alkylbenzenesulfonates. The benzenesulfonate has no alkyl portion while the p-toluenesulfonate has just one

methyl group in a position para to the sulfonate group on the benzene ring. The steady decline in the rate of adsorption with increasing molecular weight of the solute is apparent.

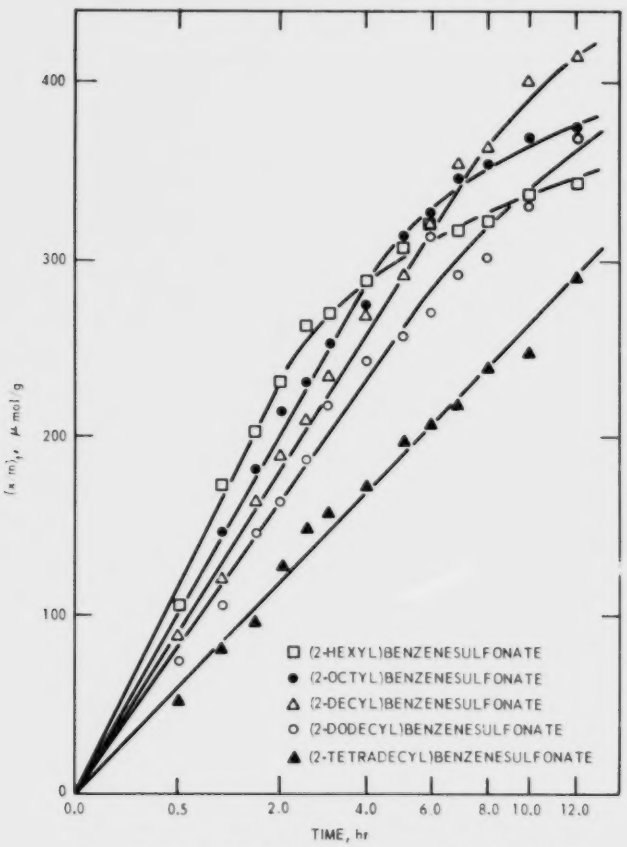

Figure 10. Effect of alkyl chain length on the rate of adsorption of alkylbenzenesulfonates (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon).

A rather broad spectrum of molecular sizes has been considered, and, as illustrated in Figure 12, a remarkable linear dependence exists between the observed k values and molecular weight. It is not possible to forecast or describe the orientation of a diffusing molecule relative to the walls of a pore channel, but it appears that by decreasing the length of the hydrocarbon chain it is possible to enhance the rate of diffusion. The

data indicate that the effect of each methylene group of the alkyl chain is linearly additive within the experimental range and that the effect of the chain length cannot, therefore, be explained entirely on the basis of physical hindrance to diffusion unless rigid configuration of the molecule is assumed.

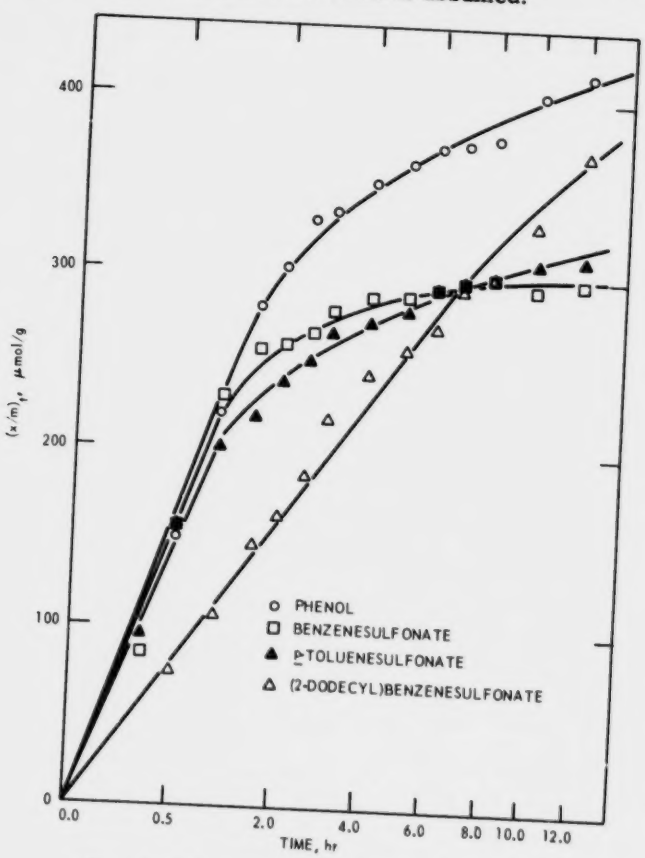

Figure 11. Effect of molecular size on rate of adsorption (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon).

If the methylene group contributes to the energy with which the molecule is adsorbed to the sides of the pore channel, it is possible that the frequency of site-to-site movement of the molecule is decreased, which decreases the rate of transport of the solute along the channel. This speculation is qualitatively in accord with the generalization that is often referred to as

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Traube's Rule. [6] The properties of amphipathic molecules having hydrophobic and hydrophilic components tend to change regularly with the length of the hydrophobic chain in a homologous series. The expulsion of increasingly large hydrophobic components from water permits an increasing number of water-water bonds to reform. Hence, the extent of adsorption from aqueous solution should generally increase regularly with the addition of CH_2 groups to the hydrocarbon chain.

When the amount of solute adsorbed is expressed in weight units instead of molar units, as in Table 3, the k values for the various pure alkylbenzenesulfonates listed are nearly the same. To a first approximation, then, the rate of adsorption of commercial detergents by carbon when computed on a weight basis may be expected to be relatively independent of the specific composition of the detergent.

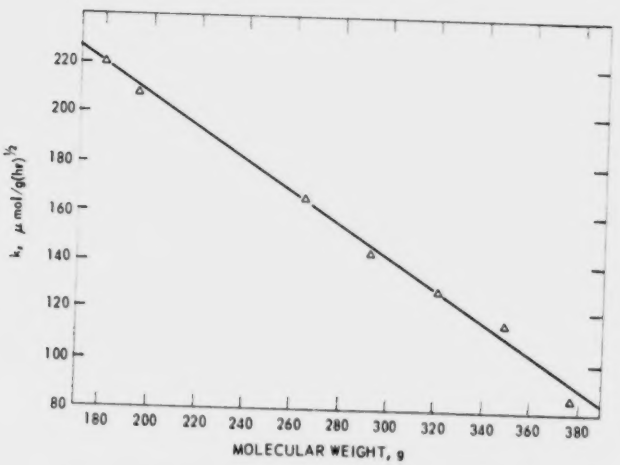

Figure 12. Effect of molecular size on rate of adsorption (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon).

Molecular Configuration of Substrate

The effects of molecular shape on the rate of uptake of ABS on granular activated carbon was studied further by determining the relative rates of adsorption of alkylbenzenesulfonates having the same molecular weight but different structures of the alkyl chains.

Table 3. RELATIVE RATES OF ADSORPTION OF PHENOL AND ALKYLBENZENESULFONATES (23 TO 25 μM INITIAL SOLUTE CONCENTRATIONS, 30°C, 35.0 mg/liter, 0.126 mm COLUMBIA LC CARBON)

Solute	k, μmol/g(hr)$^{1/2}$	kM, mg/g(hr)$^{1/2}$
Phenol	232	21.8
Benzenesulfonate	220	39.6
p-toluenesulfonate	208	40.3
(2-hexyl)benzenesulfonate	166	43.8
(2-octyl)benzenesulfonate	144	42.0
(2-decyl)benzenesulfonate	129	41.3
(2-dodecyl)benzenesulfonate	118	41.1
(2-tetradecyl)benzenesulfonate	85	32.0

Results of these experiments are given in Figure 13. It is to be noted that the structure of the alkyl chain attached to the benzene ring has a small but measurable influence on the rate of adsorption. The k value for (2-dodecyl)benzenesulfonate, in which the linear side chain is attached to the benzene ring near one extremity of the chain, is significantly greater than that for (6-dodecyl)benzenesulfonate, in which the attachment is near the center of the hydrocarbon chain. The k value for (3-dodecyl)benzenesulfonate is intermediate. Presumably the chains of the (2-dodecyl)- and (3-dodecyl)benzenesulfonates are more able to coil to form a compact and thus a more rapidly diffusing structure than is the bifurcated chain of the (6-dodecyl)-benzenesulfonate.

If this explanation is tenable the k values for technical ABS are expected to be less than those obtained for the pure materials studied since the alkyl chains of the technical products are extensively branched, a factor that would tend to inhibit flexibility and attainment of compactness. This prediction is borne out by the data presented in Table 4 for technical ABS with an average molecular weight nearly equal to those of the dodecylbenzenesulfonates.

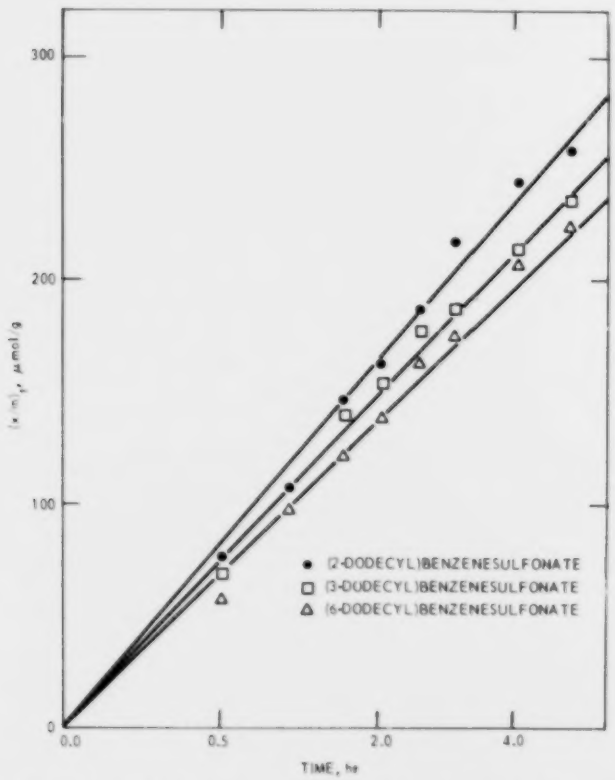

Figure 13. Effect of molecular configuration on rates of adsorption of dodecylbenzenesulfonates (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon).

Table 4. RELATIVE RATES OF ADSORPTION OF SEVERAL DODECYLBENZENESULFONATES (23 TO 25 μM INITIAL SOLUTE CONCENTRATIONS, 30°C, 35.0 mg/liter, 0.126 mm COLUMBIA LC CARBON)

Solute	k, μmol/g(hr)$^{1/2}$
(2-dodecyl)benzenesulfonate	118
(3-dodecyl)benzenesulfonate	106
(6-dodecyl)benzenesulfonate	96
Technical dodecylbenzenesulfonate	52

Rates of Adsorption of Nitrochlorobenzenes and Octylphenoxyenneaethoxyethanol

A pattern of adsorption similar to that for ABS and phenol has been observed for several other solutes, including ortho- and para-nitrochlorobenzenes and octylphenoxyenneaethoxyethanol (Triton X-100).

Studies with 50 milligrams of 0.503 millimeter carbon per liter and 50 micromolar solutions of several solutes showed that the ortho- and para-nitrochlorobenzenes exhibit much higher k values than do alkylbenzenesulfonates -values even higher than those of phenol, as illustrated in Figure 14; octylphenoxyenneaethoxyethanol was adsorbed at about the same molar rate as sodium dodecylbenzenesulfonate even though its molecular weight is nearly twice as great.

The offsets in the extrapolated zero-point adsorption found with the more rapidly adsorbed solutes may indicate a lag in complete wetting of the carbon particles or a rate-limiting step of diffusion in the solution phase for the first few minutes of reaction. The latter explanation would apply to the phenomenon of rapid, severe depletion of solute in the zones immediately adjacent to the adsorbent if the initial adsorption is extremely rapid.

EFFECTS OF PARTICLE SIZE AND CONCENTRATION OF CARBON ON RATES OF ADSORPTION

Particle Size

The rate of heterogeneous reaction such as adsorption of a solute at a solid surface may be expected to vary with the surface area and thus, for a constant weight of adsorbent, with the particle size. Hence the rate of adsorption of ABS should show a monotonic increase with some function of the inverse of the diameter of the carbon particles. The granular particles employed in this research were found upon microscopic examination to have approximately a cylindrical shape. Mathematical considerations indicate that if the mechanism of uptake is simply one of adsorption on specific external sites, the rate should vary reciprocally with the first power of the diameter, whereas for radial intraparticle diffusion the variation should be with the reciprocal of the square of the diameter (radial diameter).

Figure 15 illustrates rates of adsorption of (3-dodecyl)benzenesulfonate by different-sized particles of granular Columbia

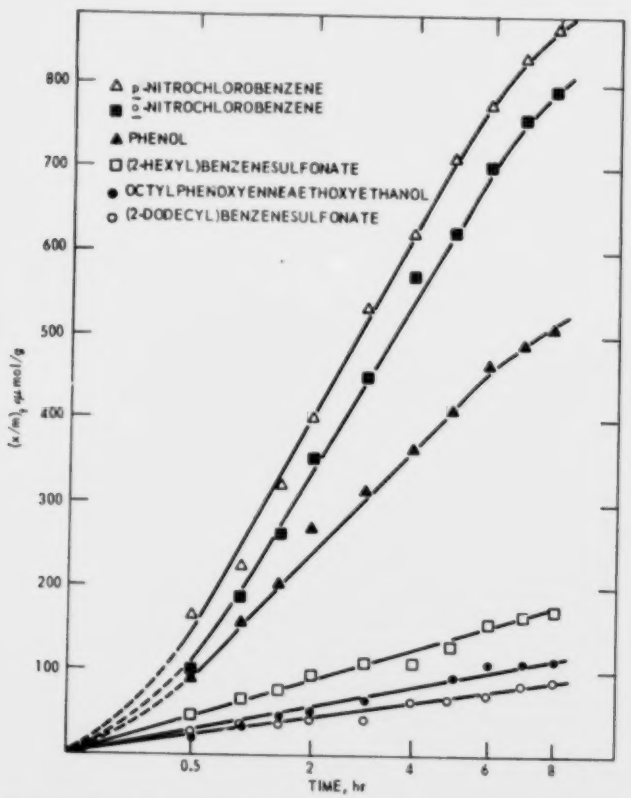

Figure 14. Rates of adsorption of selected solutes by activated carbon (30°C, 50 mg/liter, 0.503 mm Columbia LC Carbon, C_o = 50 μmol/liter).

Carbon. The particle diameters shown are averages of the mesh sizes for the sieves passing and retaining the particles. Microscopic measurements of several hundreds of individual particles for the 50/60-size carbon gave an average diameter within 2 percent of the computed value. It is apparent from Figure 15 that the relative rates conform extremely well to the idea that intraparticle diffusion is the rate-limiting step, exhibiting rate variation as a function of the inverse diameter squared.

Breaking up a large particle into smaller ones probably introduces a secondary effect of opening some tiny, sealed channels in the carbon, which then become available for diffusion

and adsorption, and thus slightly increase the specific area of a given weight of activated carbon. This effect was noted in studies of 0.273- and 0.126-millimeter carbon particles. The secondary effect is rather small, however, and can be neglected for most practical purposes within the range of particle sizes used in this research.

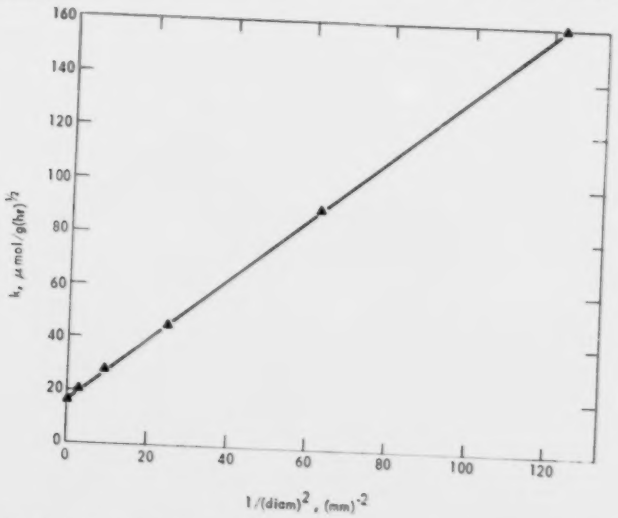

Figure 15. The effect of particle size on rate of adsorption by Columbia Carbon (25°C, C_o = 13.9 μM [3-dodecyl] benzenesulfonate).

Concentration of Carbon

It would appear that the rate of adsorption of ABS by carbon particles of a fixed size should vary linearly with the concentration of carbon in the system over a range of concentrations of carbon that does not cause great differences in the concentration of the solute remaining in solution. Large differences in the concentration of residual solute would of course introduce a second variable. Within this range then, the product of k times m, the concentration of carbon, should vary linearly with m.

Figure 16 shows rates of uptake of (3-dodecyl)benzenesulfonate from solutions of C_O = 13.1 micromoles per liter for several concentrations of carbon. The uptake is depicted in terms of total amount of solute (in units of μmol/liter) removed from solution as a function of time. The slopes of the lines of Figure 16 represent the product, km. The values for these slopes plotted as a function of m are shown in Figure 17, where

it is obvious that the effect of carbon concentration follows very well the expected behavior.

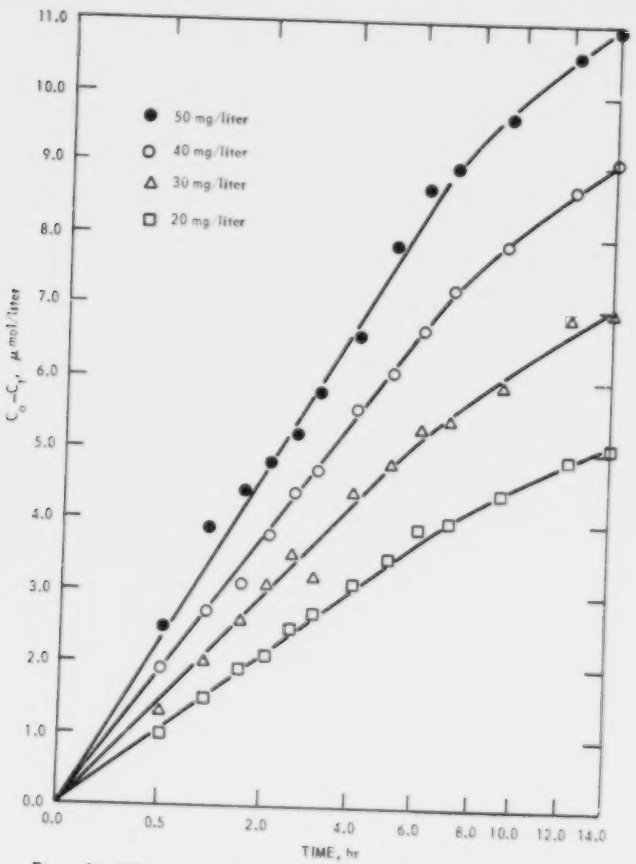

Figure 16. Effect of concentration of carbon on rate of adsorption (40°C, [3-dodecyl] benzenesulfonate, 0.200 mm Columbia Carbon).

RATES OF DESORPTION

The rate at which desorption of ABS from carbon proceeds was also studied. Different quantities of activated carbon were brought to adsorptive equilibria in concentrated solutions of (3-dodecyl)benzenesulfonate (C_O = 88.5 μmol/liter) and were then removed from these solutions and immersed in distilled water. The rate at which the solute was released by each batch of carbon was observed by the same procedure employed in studies of rates of uptake of solute by carbon.

The curves shown in Figure 18 indicate the approach of each batch to a steady-state condition. It may be noted that the times required for the desorption process to reach steady state are somewhat shorter than those required to achieve steady state conditions for uptake of the solute.

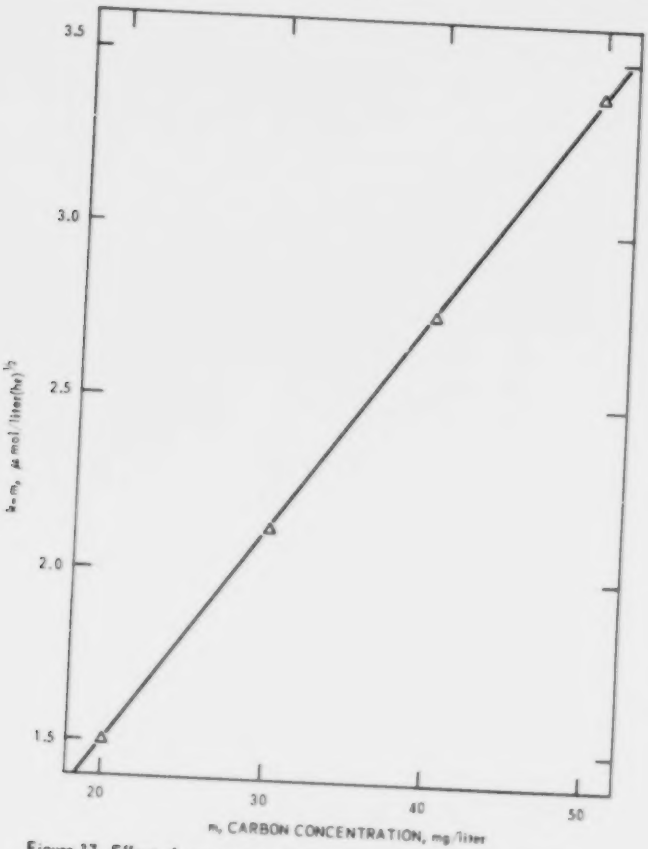

Figure 17. Effect of concentration of carbon on rate of adsorption (40°C, [3-dodecyl] benzenesulfonate, 0.200 mm Columbia Carbon).

ADSORPTION EQUILIBRIA

Reversibility

In previous discussion the approach to steady-state conditions for the process of adsorption of ABS on carbon has been described as gradual, requiring as much as several weeks for the

attainment of steady-state adsorption of the long-chain compounds. Consequently, there was some question whether the conditions reached after this time represented true positions of equilibrium. This question has been resolved by showing the reversible behavior of the adsorption.

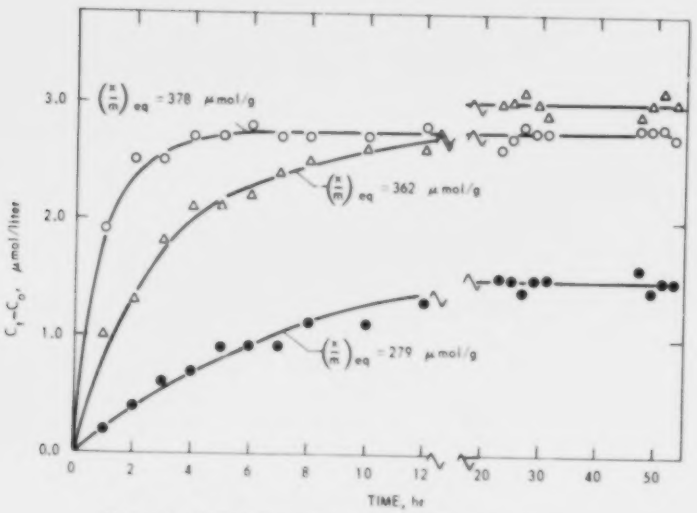

Figure 18. Rates of desorption of (3-dodecyl)benzenesulfonate (30°C, 1.420 mm Columbia Carbon).

That the adsorption of ABS on carbon is reversible is certain, as has been demonstrated by experiments described earlier. The experimental isotherms can be shown to represent equilibrium conditions if the isothermal steady-state position for desorption is found to be the same as that for adsorption, the measure of this being the degree of accord between X values, corresponding to the same concentrations of solute, for the forward and reverse processes.

The procedure used for approach to the steady state by adsorption has been outlined earlier; approach to the steady state by desorption was studied by saturating several samples of carbon with (3-dodecyl)benzenesulfonate by shaking them for many days with solutions at concentrations near 20 micromoles per liter, by separating the carbon particles from the solutions, by immersing the samples of carbon in bottles of distilled water,

and by agitating the bottles until a steady-state concentration of detergent was observed in the liquid in each bottle.

The final conditions for the desorptive steady state are represented by the triangles in Figure 19 and those for the adsorptive steady state are shown by the circles. The agreement of the data for the reverse process with those for the adsorptive uptake is satisfactory in view of the considerably greater experimental uncertainties encountered in the desorption experiments, and indicates that the experimental isotherms for adsorption represent true conditions of equilibrium.

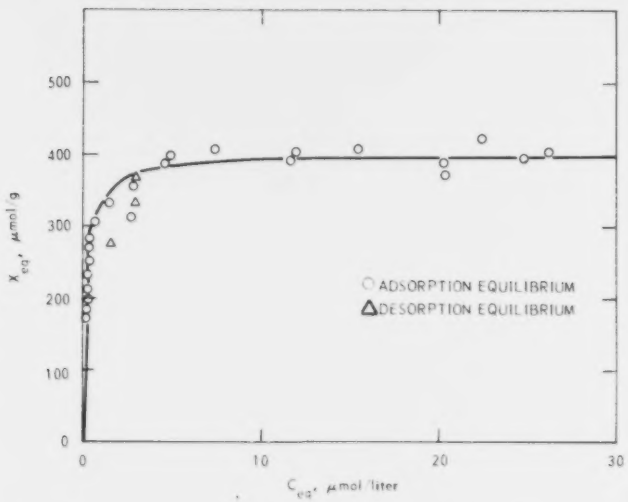

Figure 19. Adsorption isotherm for (3-dodecyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon; curve computed from Langmuir equation).

Adsorption Isotherms

The extent of utilization of the full surface area of an activated carbon for adsorption of a solute depends on the concentration of the solute in the solution with which the carbon is mixed. The relationship between the concentration of solute and the degree of its removal from solution by an adsorbent at constant temperature is called the adsorption isotherm.

Adsorption isotherms on granular Columbia Carbon for all of the alkylbenzenesulfonates studied have been determined. In addition, isotherms for phenol were measured. The levels of

uptake of the alkylbenzenesulfonates by Columbia Carbon were determined for micromolar concentrations of solute, since these cover the range of interest for water renovation. Moreover, at concentrations greater than about 10^{-4} molar the compositions of long-chain ABS solutions are considerably altered by the aggregation of individual solute ions into large ionic structures referred to as micelles. The behavior of solutions containing micelles differs vastly from that of simple solutions, and so is not particularly pertinent to concentrations of ABS found in waters and waste waters, which are considerably lower than those at which micelle formation is initiated.

An adsorption isotherm for (3-dodecyl)benzenesulfonate at 30°C has already been given in Figure 19. Comparison of Figure 19 with Figure 20, which shows a similar isotherm for (2-hexyl)-benzenesulfonate, reveals that the longer chained (3-dodecyl)-benzenesulfonate attains apparent saturation at a lower concentration. That there is a regular tendency for a leveling of adsorption to occur at a lower concentration with increasing length of the hydrocarbon chain of ABS is further evident in the isotherms for (2-octyl)-, (2-decyl)-, (2-dodecyl)-, and (2-tetradecyl)benzenesulfonates, given in Figures 21, 22, 23, and 25 respectively. Benzenesulfonates, with no alkyl component, and p-toluenesulfonate, with just a methyl group attached to an aromatic ring, provide even more marked illustration of this tendency, as shown by Figure 26.

The concentration at which a plateau-like region of the isotherm is reached is apparently not affected to any great extent by the position of attachment of the aromatic portion of the adsorbate molecule to the alkyl chain; this may be observed by comparison of the isotherm for (3-dodecyl)benzenesulfonate (Figure 19) with those for (2-dodecyl)- and (6-dodecyl)benzenesulfonate (Figures 23 and 24).

Each point on the adsorption isotherms shown in Figures 19 through 26 represents an independent adsorption experiment, carried to steady state or equilibrium conditions. The first step in these experiments was to determine the time required to attain adsorption equilibrium on 0.273 millimeter Columbia Carbon for each solute. These times ranged from approximately 1 week for phenol, benzenesulfonate, and p-toluenesulfonate to 4 weeks for the long-chain compounds such as dodecylbenzenesulfonate and tetradecylbenzenesulfonate. Then, for each experiment, a quantity of carbon was weighed accurately and placed in a 300-milliliter reaction vessel containing 250 milliliters of a solution of solute, whose concentration had been measured precisely. The vessel was then

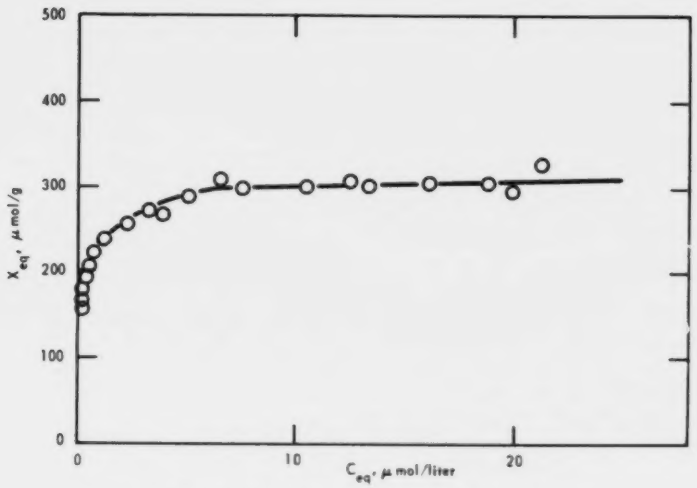

Figure 20. Adsorption isotherm for (2-hexyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

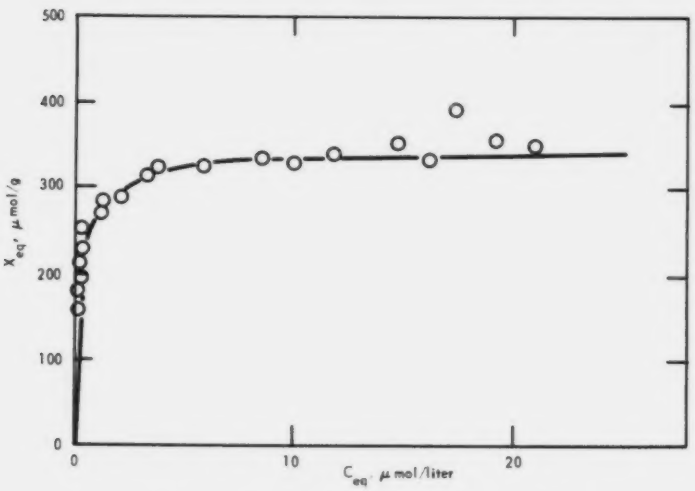

Figure 21. Adsorption isotherm for (2-octyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

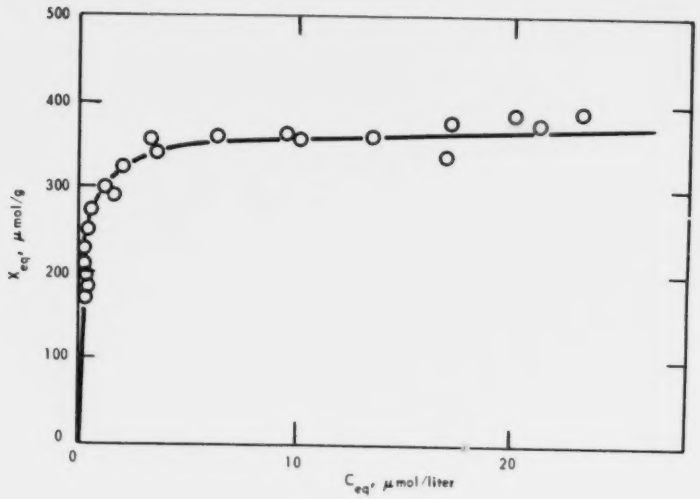

Figure 22. Adsorption isotherm for (2-decyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

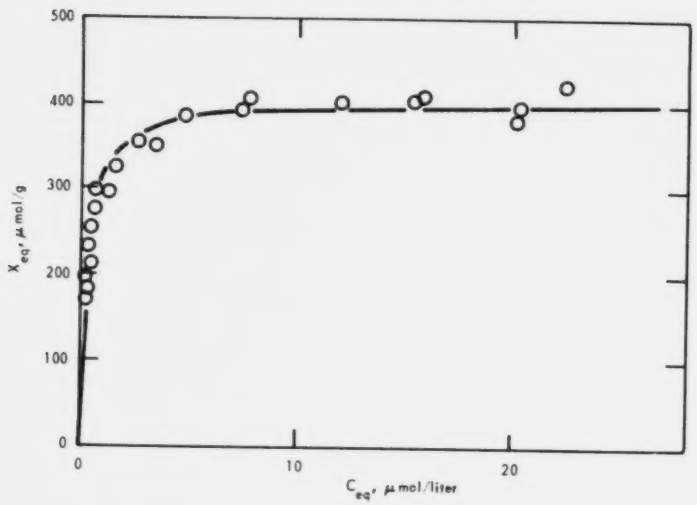

Figure 23. Adsorption isotherm for (2-dodecyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

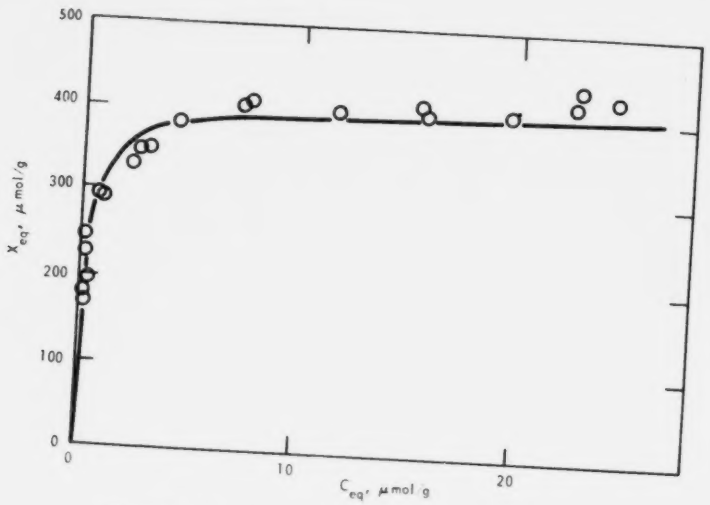

Figure 24. Adsorption isotherm for (6-dodecyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

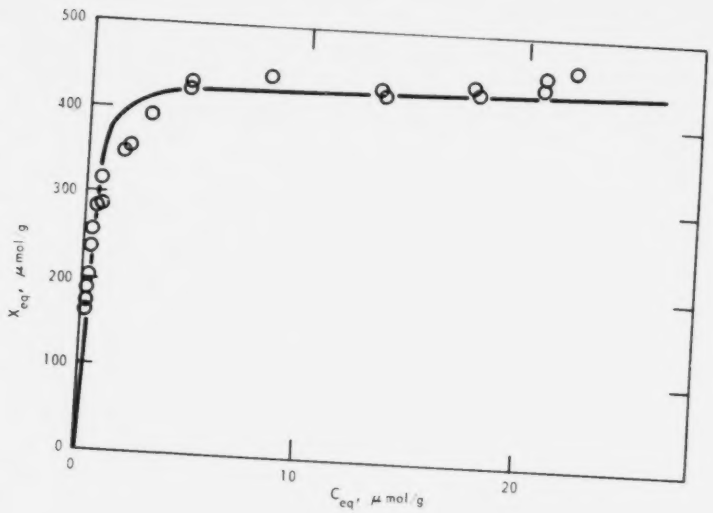

Figure 25. Adsorption isotherm for (2-tetradecyl)benzenesulfonate (30°C, 0.273 mm Columbia Carbon. Curve computed from Langmuir equation).

sealed and placed in an oscillating shaker. After the appropriate time had elapsed, the flask was removed and the concentration of solute remaining in solution was determined. The flask was then resealed and placed back in the shaker for an additional 3 days; another determination of the concentration of residual solute was then made to insure that equilibrium had been reached. If the second reading did not agree with the first, the vessel was replaced in the shaker for another 3 days. This was necessary in only one instance, when a solution of relatively large concentration of tetradecylbenzenesulfonate was being studied.

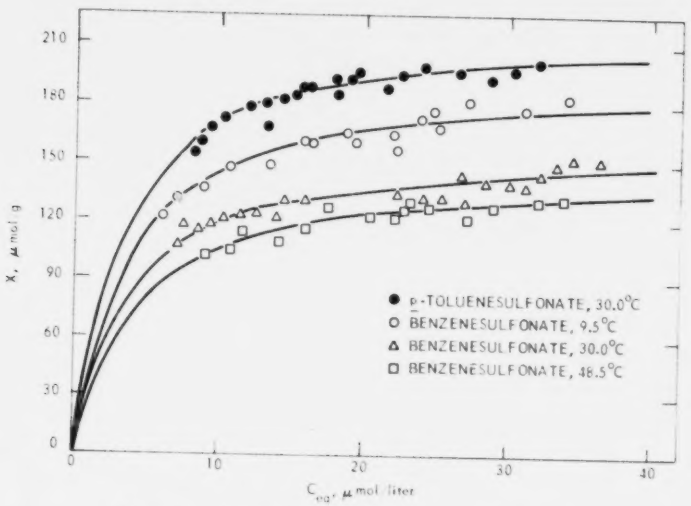

Figure 26. Adsorption isotherms for benzenesulfonate and p-toluenesulfonate (0.273 mm Columbia Carbon. Curves computed from Langmuir equation).

The amount of solute adsorbed by the carbon in the flask was then divided by the weight of the carbon to give one value of X for the isotherm. Each experimental value of X was so determined. Values of X covering the range of concentrations of interest for waste-water renovation were obtained by varying the amount of carbon and the initial concentration of solute.

Adsorption isotherms for phenol were also determined, for capacity for the adsorption of phenol is often used for estimation of the surface properties of carbon. Moreover, phenolic materials comprise another undesirable class of compounds that occurs frequently in waste waters and water supplies. In addition, detailed isotherms for the adsorption of phenol on numerous types

of carbon have been reported and provide a good basis for comparison of the present work with that of others. [7] Most of the significant fundamental work on the adsorption of phenol from aqueous solutions by carbon has been conducted with solute concentrations near 10 percent of saturation. Since, like ABS, phenol occurs in waters and waste waters in only micromolar concentrations, fundamental studies directed toward water renovation must cover also this lower concentration range. In view of the dependence of extent of adsorption on concentration, detailed experiments with phenol were carried out for both the micromolar and millimolar ranges of concentration to permit estimation of the fraction of active surface that can be considered as useful over a practical range of concentrations as compared with the active surface utilized in nearly saturated solutions.

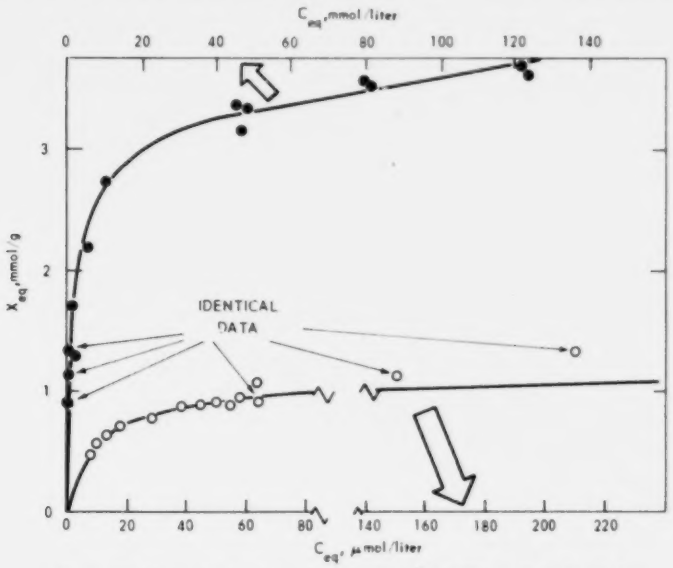

Figure 27. Adsorption isotherms for phenol (30°C, 0.273 mm Columbia Carbon. Curves computed from equations).

The data from equilibrium studies for both concentration ranges are plotted in Figure 27. Note that for each range of concentration the phenol exhibits an isotherm of typical shape, the curvature observed in the experiments at low concentration being completely concealed in the plot covering the experiments at high concentrations because of its compression within the first few divisions on the scale of concentration. Continuous

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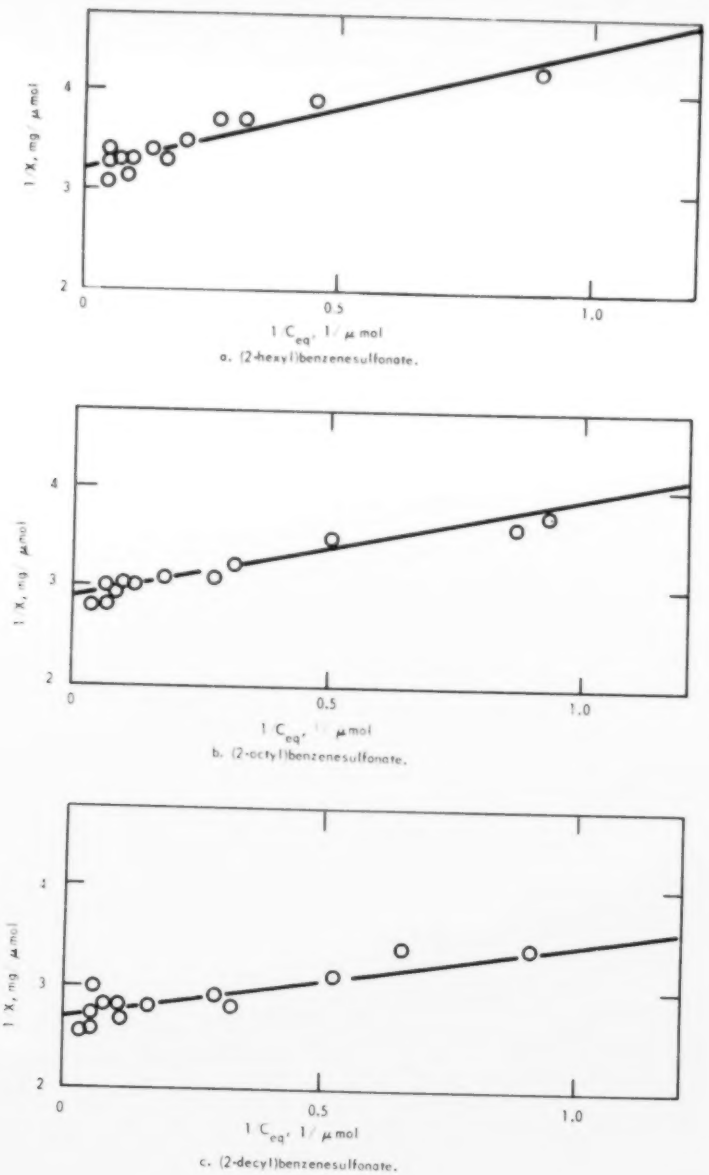
curvature of this sort over several orders of magnitude in concentration is not subject to rigorous interpretation by the common simplified equations for adsorption equilibria. Interpretation requires postulation of a range of activities for various portions of the surface area, a concept partially in accord with the B.E.T. theory.

Interpretation of Experimental Adsorption Isotherms

Preferred formulations for mathematical description of adsorption isotherms are the Langmuir equation, $X = X_m\, bC/(1+bC)$, and the B.E.T. equation, $X = X_m\, AC/(C_s-C)\,[1 + (A-1)\,C/C_s]$. The pattern of the experimental isotherms for the alkylbenzenesulfonates shown in Figures 19 through 26 is qualitatively similar to the form of the Langmuir equation, and in fact, the data were found to be well described quantitatively by this equation. Plots of 1/X against 1/C are shown for the individual alkylbenzenesulfonates in Figures 28, 29, and 30, and can be seen to conform nicely to the linearity predicted by the Langmuir equation. From the slopes and intercepts of the straight lines fitting these data, the values of the two parameters, X_m and b, of the Langmuir equation were calculated; these values are presented in Table 5.

Table 5. CONSTANTS OF LANGMUIR EQUATION FOR ADSORPTION ISOTHERMS (30°C, 0.273 mm COLUMBIA CARBON)

Compound	X_m, mg/g	X_m, mmol/g	b, 1/μmol	Area per molecule, $A^{o\,2}$
Phenol (C_{eq} = 5-210 μmol/liter)	103	1.09	0.108	(41.2)
Benzenesulfonate	29	0.161	0.282	280
p-toluenesulfonate	43	0.222	0.334	200
(2-hexyl)benzenesulfonate	83	0.313	2.56	140
(2-octyl)benzenesulfonate	101	0.345	2.90	130
(2-decyl)benzenesulfonate	119	0.370	3.60	120
(2-dodecyl)benzenesulfonate	139	0.400	4.55	110
(3-dodecyl)benzenesulfonate	139	0.400	4.63	110
(6-dodecyl)benzenesulfonate	139	0.400	4.55	110
(2-tetradecyl)benzenesulfonate	164	0.435	6.76	100



a. (2-hexyl)benzenesulfonate.

b. (2-octyl)benzenesulfonate.

c. (2-decyl)benzenesulfonate.

Figure 28. Langmuir plots of adsorption isotherms (0.273 mm Columbia Carbon, 30°C).

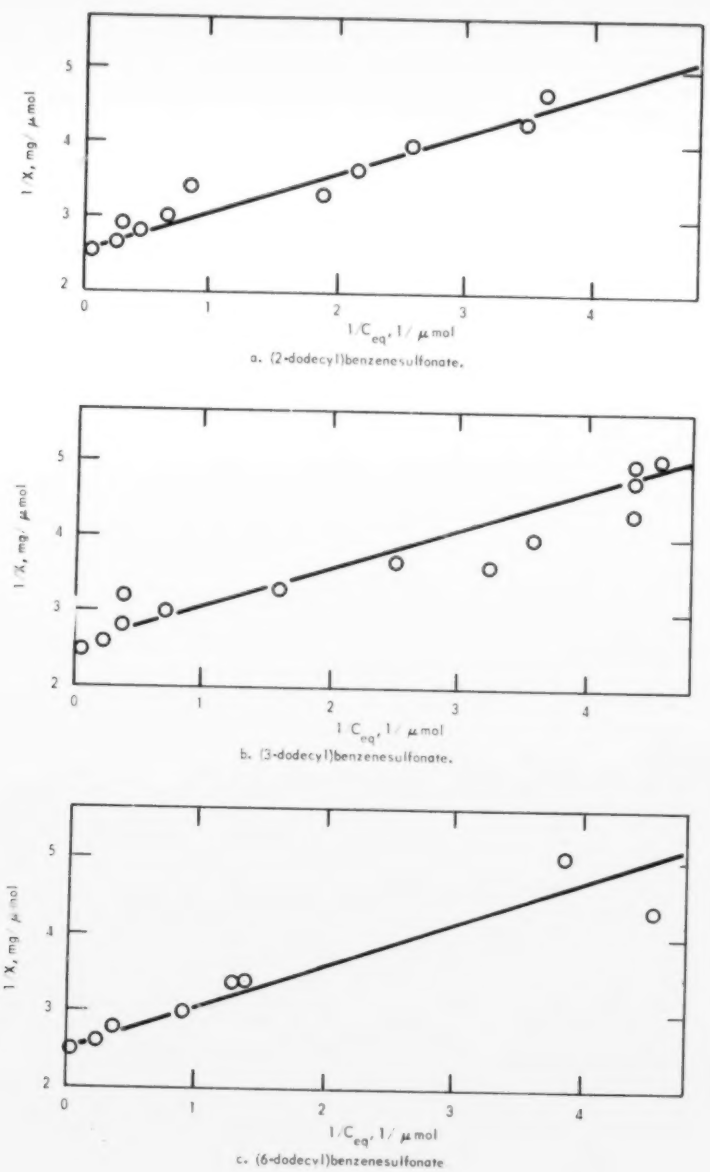
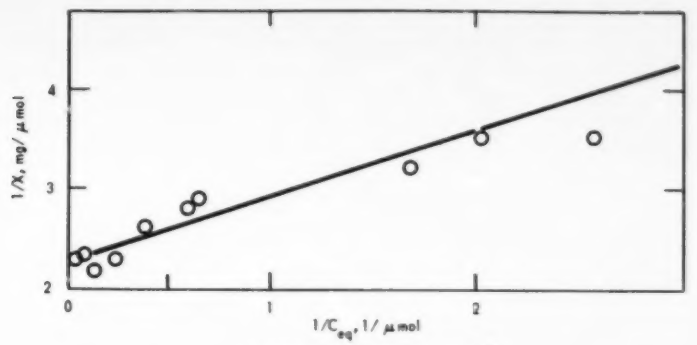
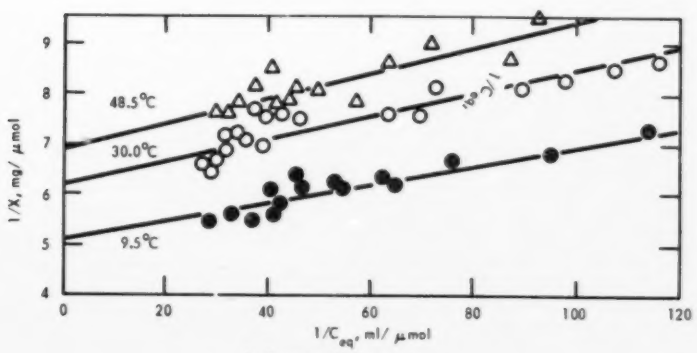


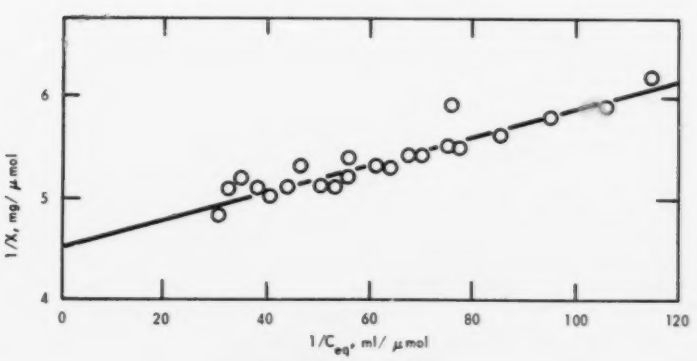
Figure 29. Langmuir plots of adsorption isotherms (0.273 mm Columbia Carbon, 30°C).



a. (2-tetradecyl)benzenesulfonate, 30°C.



b. benzenesulfonate.



c. p-toluenesulfonate, 30°C.

Figure 30. Langmuir plots of adsorption isotherms (0.273 mm Columbia Carbon).

The data for the lower concentration range for phenol were also correlated with the Langmuir equation, the linearization of the data being excellent when 1/X is plotted as a function of 1/C, as shown in Figure 31. The values of X_m and b for the low-concentration isotherm for phenol are also given in Table 5.

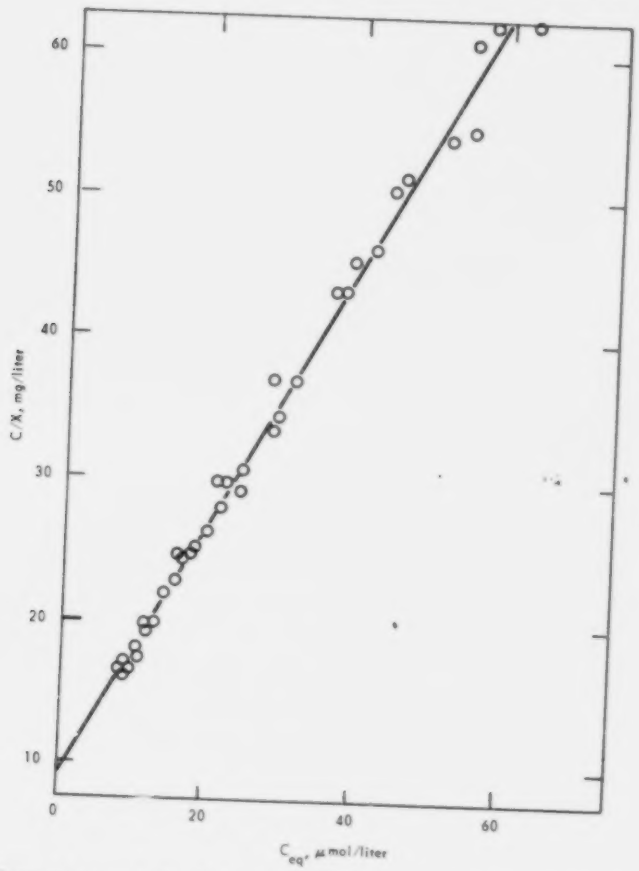


Figure 31. Langmuir plot of adsorption isotherm for phenol (30°C, 0.273 mm Columbia Carbon; C_{eq} <220 μmol/liter).

It will be recalled that X_m, according to the Langmuir equation, is the limiting amount of adsorbed material required to give a complete monolayer on the surface and that b, the reciprocal of the concentration at which half-coverage is attained, is a measure of the relative adsorptive affinity.

Equilibrium Capacities and Adsorptive Tendencies

The values of b in the fourth column of Table 5 reflect the steepness of the approach to saturation of the available surface of the carbon with respect to the concentration of solute. The values of b for the alkylbenzenesulfonates increase regularly with increased size of the alkyl chain, indicating a greater tendency toward adsorption. For the dodecylbenzenesulfonates the concentration in solution corresponding to half-saturation is only 0.22 micromole per liter or about 0.08 milligram per liter as opposed to roughly 8 micromoles per liter or nearly 0.8 milligram per liter for phenol. Qualitatively it may be concluded that the respective adsorptive affinities for alkylbenzenesulfonates and for phenol differ by an order of magnitude.

The much smaller monolayer capacity of benzenesulfonate in comparison with that of phenol, as shown by the values of X_m in Table 5, is somewhat surprising. This decreased capacity may reflect mutual repulsion by the ionic sulfonate groups of the latter compound so that they are not able to pack nearly as closely on the surface as can the phenol molecules. Then the increase in capacity with increasing size of the alkyl group on the benzene ring may be partly the result of an insulating effect so that closer packing becomes possible. It may also indicate enhancement of adsorptive properties owing to the increasing number of water-water bonds that are permitted to reform upon removal from solution of solute molecules with increasing numbers of methylene groups, as discussed previously.

Although the capacities of the dodecylbenzenesulfonates, which are most nearly like commercial detergents, are only about 40 percent of the capacity of phenol on a molar basis, they are significantly greater on a weight basis, as shown in the second column of Table 5. The larger area per molecule, derived from the molar capacity, is to be expected if the large alkyl groups are occupying surface area.

The capacity figures on a weight basis show that it may be possible to adsorb as much as 15 percent by weight of detergent with the experimental carbon. This extent of adsorption is approached at equilibrium for concentrations of solute in the range of the plateaus of the adsorption isotherms. At concentrations less than those for which adsorption approaching apparent monolayer saturation of the carbon obtains, smaller amounts of solute are adsorbed by a given weight of carbon. Consequently, more efficient utilization of carbon will occur by employing column-type operation rather than batch treatment in waste-water renovation. The concentrations of ABS and other organic contami-

nants in waters and waste waters are usually small, in the range from approximately 2 or 3 to 50 micromoles per liter. In batch operation even these concentrations would be lessened considerably as the process proceeds, and at equilibrium are likely to be much less than any concentration giving adsorption near that of the plateau of the adsorption isotherm. In fact, effluent waters should desirably contain less than approximately 0.1 milligram ($< 0.3\ \mu$mol/liter) of ABS per liter, and this requirement dictates operation of batch treatment at a relatively inefficient position on the adsorption isotherm. Consequently, full utilization of the carbon will not be achieved in a batch process. Column operation, on the other hand, provides for a nearly constant concentration of solute in the solution in initial contact with the adsorbates; the solution in contact with the first section of carbon in the column has a concentration very nearly equal to that in the influent. Column operation is then likely to insure much more effective utilization of the capacity of the carbon by virtue of the way in which the solution makes contact with the carbon.

pH Effects

The pH of the solution from which adsorption of ABS on activated carbon takes place has an effect not only on the rate of adsorption but also on the equilibrium uptake. Values of **X** for the adsorption of (3-dodecyl)benzenesulfonate on carbon at equilibrium concentrations in the range of 5 to 10 micromoles per liter and at selected values of solution pH are shown in Figure 32. This alkylbenzenesulfonate exhibits greater affinity for Columbia Carbon at low pH values, the affinity increasing regularly with increasing hydrogen ion concentration over the range of pH values common to waters and waste waters, and increasing somewhat more sharply with decreasing pH below pH 4.

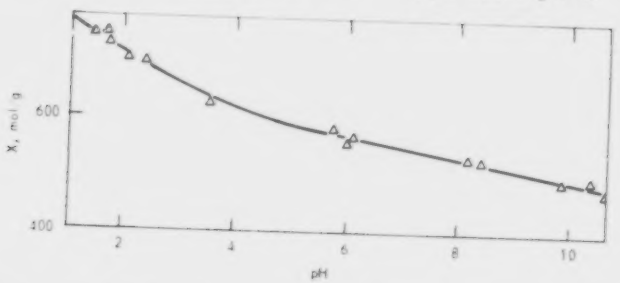


Figure 32. Effect of pH on adsorption equilibria ([3-dodecyl] benzenesulfonate, 30°C, 32.0 mg liter, 0.126 mm Columbia Carbon).

The increase in affinity with decrease in pH noted for adsorption equilibria accords with observations on increasing rates of uptake of ABS with decreasing pH. Since the ionic species of ABS are negatively charged, enhanced adsorption at low pH may result from neutralization of negative charges at the surface of the carbon with increasing hydrogen ion concentration, which reduces hindrance to diffusion and also makes available more of the active surface of the carbon. This effect would be expected to vary in degree for different carbons, for the charges at the surfaces of the carbon depend upon the composition of the raw material used for preparing the activated carbon and upon the technique of activation. Further testing of pH effects on the adsorption of neutral molecules and cations on the Columbia Carbon should give evidence of the reasonableness of this proposal. Triton X-100, a nonionic detergent, is an example of the type of adsorbate that could be used for the testing. Electrophoretic measurements on individual carbon particles is another experimental technique that should yield information about the net charge on the surface of the carbon. These studies will be included in future extension of the present work.

Effect of Temperature

The process of adsorption of benzenesulfonate on activated carbon seems sufficiently similar to that of ABS that the effect of temperature on the adsorption of the simpler compound is useful as a general indication of behavior, at least qualitatively. So the faster reacting benzenesulfonate-activated carbon system was employed for estimating the effect of temperatures upon adsorption equilibria of ABS on carbon.

In Figure 26 are plotted the data from studies with this system at 9.5°C, 30.0°C, and 48.5°C. Contrary to the effect of temperature on rates of adsorption, the X value, at equilibrium, for a given value of C is seen to increase with decreasing temperature. This finding is directly in accord with the Gibbs equation for equilibrium conditions, and so is not unexpected.

Figure 30b illustrates the conformity of the data at each temperature to a Langmuir isotherm; the parameters for the Langmuir equation have been computed and are tabulated in Table 6.

Temperature effects on adsorption equilibria are generally felt to be not significant, particularly over the range of temperature encountered in water and waste waters. This fact is evidenced by the values of X_m and b in Table 6. In practical

operations the variation in temperature will be small relative to that imposed upon the experimental system.

Table 6. CONSTANTS OF LANGMUIR EQUATION FOR ADSORPTION OF BENZENSULFONATE AS A FUNCTION OF TEMPERATURE

Temperature, °C	X_m, mg/g	X_m, mmol/g	b, 1/μmol	Area per molecule, A^{o2}
9.5	35	0.196	0.283	230
30.0	29	0.161	0.282	280
48.5	26	0.145	0.276	310

The slight increase in affinity with increasing temperature, noted in the values of X_m in Table 6, is predictable from the thermodynamic properties of adsorption. Decreasing adsorption with increasing temperature indicates that adsorption is exothermic. The change in the heat content of a system in which adsorption occurs, that is, the total amount of heat evolved in the adsorption of a definite quantity of solute on adsorbent, is termed the heat of adsorption, ΔH. Heats of adsorption on activated carbon from the gas phase are generally several kilogram calories per mole, but since water is desorbed from the surface when adsorption from aqueous solutions occurs, heat effects for the latter process would be expected to be smaller than those for gas-phase adsorption.

The differential heat of adsorption for benzenesulfonate has been determined with the values of X_m, computed from the Langmuir equation, corresponding to the selected temperatures and the van't Hoff equation in the form

$$\Delta H = 2.303\ R\ \frac{(T_1T_2)}{T_2-T_1}\ (\log X_{m,2} - \log X_{m,1}) \qquad (4)$$

The logarithms of X_m for the data from Table 6 are plotted versus the reciprocal of Kelvin temperature in Figure 33. From this plot the slope, $\Delta H/2.303\ RT_1T_2$, was taken and ΔH was computed as follows:

$$\Delta H = 2.303\ (1.986)\ (285.7)\ (312.5)\ .\ \frac{(2.184 - 2.275)}{(312.5 - 285.7)}$$

ΔH = -1,400 cal per mole

The negative sign of ΔH confirms that the adsorption is an exothermic process.

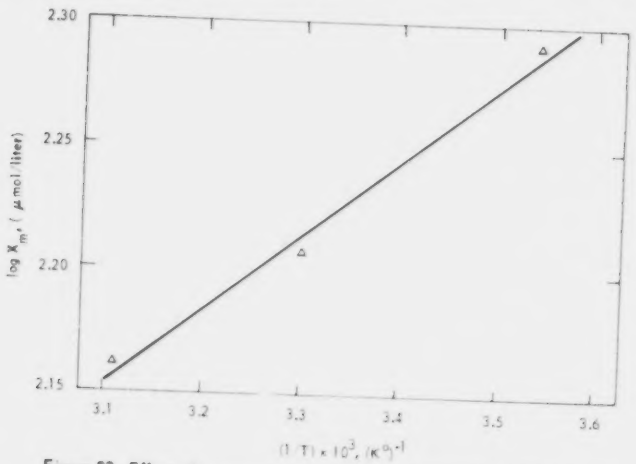


Figure 33. Effect of temperature on adsorption of benzenesulfonate on carbon (0.273 mm Columbia Carbon).

The value of 1.4 kilogram calories per mole is within the expected range for physical adsorption. Furthermore, this value accords well with the heat of solution of the benzenesulfonate, which ranges from 0.8 to 3.4 kilogram-calories per mole for the anhydrous compound and for that containing two moles of water, respectively. [8]

SPECIFIC SURFACE AREA

One method of comparing potential adsorptive capacities of solid adsorbents or of estimating mean grain size or porosity is by computation of specific surface areas. By use of an appropriate equation for the adsorption isotherm, the quantity of adsorbate required to form a complete monolayer on the surface is computed. Combination of this with some reasonable value for the area of the surface covered per molecule is then made to compute the surface area per unit of adsorbent. Gas phase measurements with adsorbates such as nitrogen, argon, and butane usually give concordant results. The method has been applied much less frequently to adsorbates in solution.

Estimations of the specific surface areas of carbons and other solid adsorbents are conventionally based upon measurements of the capacity of the adsorbent for a selected solute

having a well-accepted molecular cross-sectional area. Determinations of capacity are made by fitting either the Langmuir or B.E.T. equation to isothermal equilibrium data, for a series of concentrations usually in the range from 0.1 C_S to 0.8 C_S, (C_S = saturation concentration of solute in solution); from the fitted equation the capacity factor, X_m, is computed.

When X_m is expressed in moles per unit of carbon, the specific area, Σ, per unit of carbon can be computed from the relationship

$$X_m = \frac{\Sigma}{N \sigma^o} \qquad (5)$$

in which σ^o is the postulated cross-sectional area of a molecule of adsorbate (actually the area of carbon occupied by one molecule of solute), and N, the Avogadro number, is the number of molecules per mole.

Phenol is often used as the adsorbate upon which are based measurements of specific areas of carbons for adsorption from aqueous solutions. The cross-sectional area of the phenol molecule for adsorption is rather well established, being taken commonly as 41.2 Angstroms squared. [9] As mentioned previously, measurements are usually carried out in rather concentrated solutions; since, however, the concentrations of interest in waters and waste waters are micromolar, it appeared desirable to examine the specific surface areas observed for adsorption in this range as well as in the conventional range. That there would be some difference was shown by the need to use different equations to represent the adsorption in these two ranges of concentration. Comparison of the specific area computed from the isotherm for the low range of concentrations with that for the high range permitted estimation of the "effective" adsorptive area of the activated carbon in dilute solutions.

Two portions of the isotherm for phenol have been presented in Figure 27. Although a single equation is not adequate for both portions, the separate segments were correlated with the aid of standard equations. As shown in Figure 34, the high-range data conform well to the B.E.T. equation, an observation in agreement with those of other investigators. [7] In the micromolar region, however, the data are best described by the Langmuir equation, as is evidenced by Figure 31, with a different set of constants.

From the equation for the straight line shown in Figure 34 a value of X_m equal to 3.22 millimole per gram was computed. By using 41.2 square Angstroms as the molecular area of phenol, the

total surface area of the carbon was computed to be 800 square meters per gram, an area that accords well with measurements by others on similar activated carbons. [10]

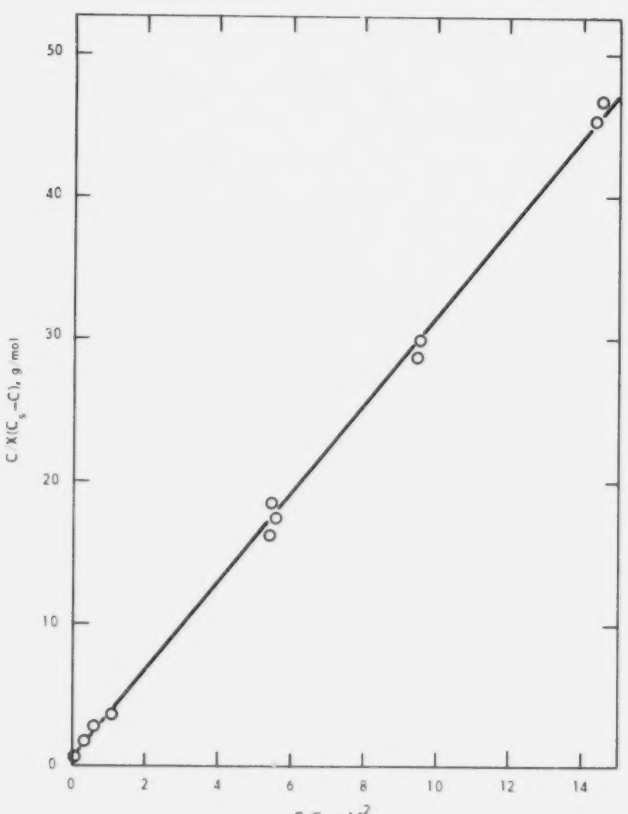


Figure 34. B.E.T. plot of adsorption isotherm for phenol (30°C, 0.273 mm Columbia Carbon, 50 μ mol liter C_{eq}, <30 mmol/liter).

The data for the lower concentration range were correlated with the linear form of the Langmuir equation. From the equation for the straight line in Figure 31 the value for X_m was calculated to be 1.1 millimole per gram, and, again by using 41.2 square Angstroms as the molecular area of phenol, the monolayer area was computed to be 270 square meters per gram or

roughly one-third of the area determined by conventional methods. This is evidence that the prediction of capacities based upon conventional measurements of specific area constitutes an overextension of data, and that care must be taken to deal only with interpolated information (or information obtained only from carefully considered extrapolation of the data) in such complex processes.

By using Equation 5 and the computed specific area value of 270 square meters per gram, the mean surface areas occupied per molecule have been computed for all of the alkylbenzenesulfonates; the values are shown in Table 5. These values are obviously somewhat high, and should not be taken as indicative of the cross-sectional areas of the respective molecules. Not enough is known about the adsorption process for materials like ABS nor about the effectiveness of mutual ionic repulsion in reducing the quantity adsorbed to evaluate the significance of the large apparent surface areas. It may be that they represent an area of exclusion of other alkylbenzenesulfonates by ionic repulsion. Increased total adsorptive capacities observed with mixed solutions of ion (ABS) and neutral molecule (phenol), discussed next, would be in accord with this view. On the other hand it may be that some of the pores of the carbon are too small for ABS to enter and so the total area available for adsorption of ABS is less than for adsorption of phenol. This interpretation is not, however, in accord with the large apparent cross-sectional area of benzenesulfonate.

The value of b for the Langmuir equation describing the adsorption of phenol at micromolar concentrations was calculated to be 0.108 micromole $^{-1}$, while the corresponding measure, A/C_S, of the free energy of interaction of phenol with the surface of the carbon at near-saturation concentrations was found to be 4.57×10^{-4} micromole $^{-1}$. The parameters b and A/C_S, which are expressive of the free energy of interaction with the surface, are measures of the "tightness" of binding between the adsorbate and the surface.

Comparison of the values of b and A/C_S for phenol indicates that the tightness of binding at small concentrations of phenol is roughly 240 times as great as that at large concentrations. This indicates that a certain percentage - probably quite small - of the available adsorptive sites on the surface of the carbon are very active relative to the remaining ones.

It is improbable that the surface is uniform in activity. Rather, there must be regions with differing degrees of affinity. For example, isolated carbon atoms along ridges or peaks on

the surface are likely to exhibit greater residual intermolecular forces, and the adsorptive affinity of such sites will consequently be relatively great. The effect of adsorption at the highly active sites is more pronounced in the range of low concentration since these places account for a greater percentage of the total number of sites on which adsorption occurs at low concentration than they do at high concentration.

COMPETITIVE ADSORPTION

General Considerations

In only specialized instances will adsorption be limited to the removal from solution of but one solute. In any practical use of activated carbon as an adsorbent for pollutants in waters, adsorption will occur from a solution containing a complex mixture of materials rather than a single pure compound. The materials in such a complex solution may mutually enhance adsorption, may adsorb relatively independently, or may interfere with the adsorption of other materials. The last of these seems most probable, for the same surface area is used at least in part for all adsorbates.

To determine more specifically the nature and magnitude of the interactions, investigations have been made with a few simple mixed solutions, which contain two solutes whose individual adsorptive properties have been studied previously. The simple systems were selected with the expectation that they would permit more quantitative elucidation of competitive effects than would more complex ones, while still providing information that could be extrapolated from laboratory studies to prospective applications.

Renn and Barada [11] at the Johns Hopkins University investigated the adsorption of ABS by powdered activated carbon. They reported no competition or interference between the adsorption of phenol and that of ABS. Unfortunately, the lack of mention of times of contact and the failure to distinguish between rates of adsorption and adsorptive equilibria make their conclusion rather meaningless.

Since the materials they used represent types of objectionable pollutants, experiments with the same materials were conducted as part of the present work, except that pure (2-dodecyl)-benzenesulfonate was used in place of technical ABS. Additional studies with mixtures of (2-dodecyl)benzenesulfonate and dodecylsulfate in solution were also performed to determine whether the competitive effects observed in the former system occurred also for solutions of other mixed adsorbates.

Both individual rates of adsorption and individual adsorptive capacities were studied for the phenol-ABS system. Only rates of adsorption were studied for the sodium dodecylsulfate-dodecylbenzenesulfonate system. Data for the adsorption of sodium dodecylsulfate alone were not obtained in these experiments because of lack of a suitable analytical method applicable to small concentrations of sodium dodecylsulfate. Consequently, only the effect of the presence of sodium dodecylsulfate on the adsorption of dodecylbenzenesulfonate was determined.

Granular Columbia LC Carbon with a mean particle diameter of 0.126 millimeter was used throughout. All experiments were conducted at 30°C.

Rates of Adsorption

Figure 35 shows the results of an experiment in which the initial molar concentration of (2-dodecyl)benzenesulfonate was roughly three-fourths of the initial concentration of phenol.

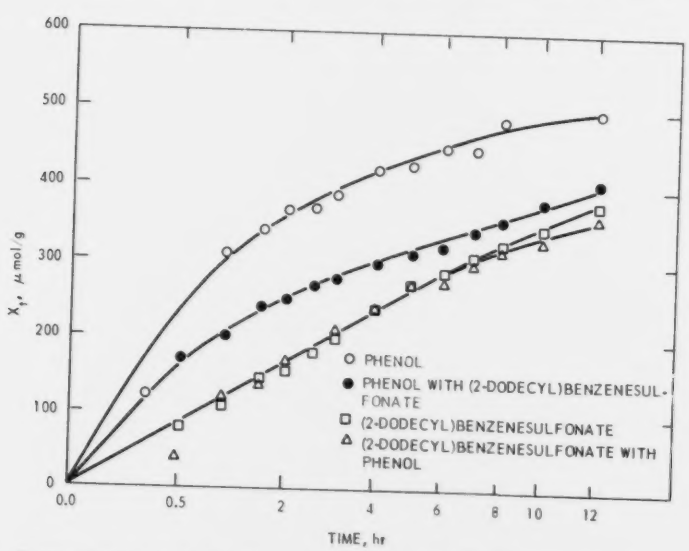


Figure 35. Rates of adsorption from a bisolute solution [(2-dodecyl) benzenesulfonate and phenol, 30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon, $(C_o)_{2\text{-dodecyl}} / (C_o)_{phenol} = 0.735$].

At this ratio of concentrations the phenol exhibited no observable effect on the rate of adsorption of the alkylbenzenesulfonate, but the rate of adsorption of the phenol was considerably reduced in

the presence of the surfactant. This indication of interference, which was much at variance with the statement of Renn and Barada, suggested that the system should be investigated in more detail. Accordingly, a more extensive series of experiments was conducted; the data from these experiments are shown in Figure 36 and in Table 7, which is a compilation of the experimental results displayed graphically in Figures 35 and 36.

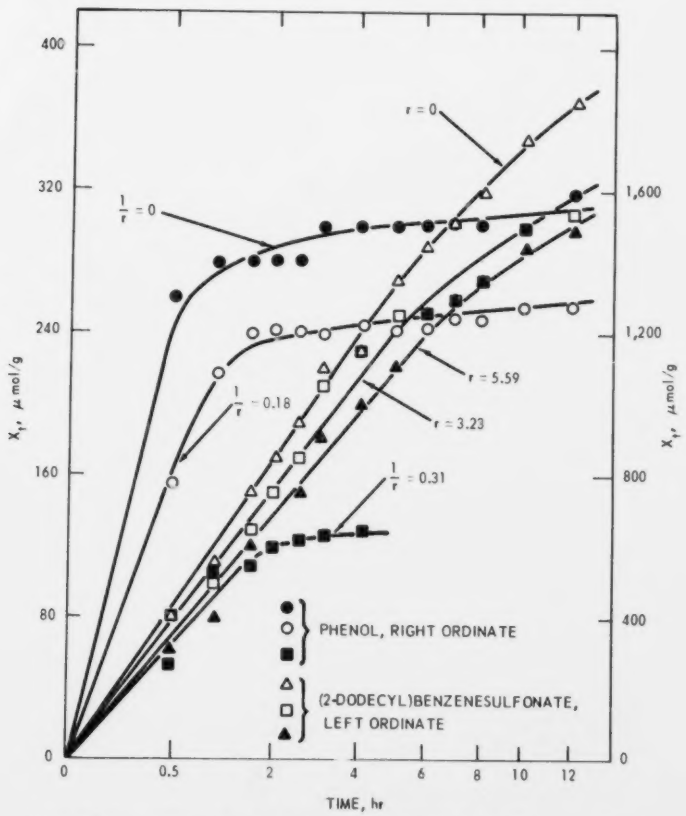


Figure 36. Competitive adsorption between phenol and (2-dodecyl)benzenesulfonate [30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon, $r = \frac{(C_o)_{phenol}}{(C_o)_{ABS}}$].

In contrast to the findings of Renn and Barada, each solute was observed to compete in some way with the adsorption of the other. Comparison of the k values in the second and third rows

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Table 7. RATES OF ADSORPTION ON CARBON FROM BISOLUTE SOLUTIONS (30°C, 35.0 mg/liter, 0.126 mm COLUMBIA CARBON)

$C_o(A)$, μmol/liter	$C_o(B)$ μmol/liter	$\frac{C_o(B)}{C_o(A)}$	k_a, μmol/g(hr)$^{1/2}$	k_b, μmol/g(hr)$^{1/2}$
Section 1: (A) represents (2-dodecyl)benzenesulfonate, (B) represents phenol				
21.9	0.0	0.00	119	-----
0.0	29.2	-----	-----	310
21.6	29.4	1.36	119	220
24.5	0.0	0.00	120	-----
23.9	77.2	3.23	110	480[a]
23.0	128.6	5.59	98	1,150
0.0	129.2	-----	-----	1,750
Section 2: (A) represents (2-dodecyl)benzenesulfonate, (B) represents sodium dodecylsulfate				
24.5	0.0	0.00	120	-----
24.5	17.3	0.71	106	-----
24.5	34.7	1.42	95	-----
24.5	52.0	2.12	82	-----

[a]In comparing this value with the others in this column the difference in the $C_o(B)$ value must be taken into account.

of the last column in Table 7 shows that the rate of adsorption of phenol from water alone was decreased to roughly two-thirds of its value in the presence of a slightly less than equimolar concentration of the (2-dodecyl)benzenesulfonate. The same type of reduction can be observed from the figures in the sixth and seventh rows of Table 7. With equimolar concentrations of phenol and ABS the rate of adsorption of the (2-dodecyl)benzenesulfonate was not measurably affected; in the presence, however, of a greater proportion of phenol the rate was retarded somewhat, as evidenced by the k values in the fourth column of Table 7.

The additional studies with mixtures of (2-dodecyl)benzenesulfonate and dodecylsulfate in solution demonstrated that this latter material also adversely affects the rate of adsorption of ABS as shown in Figure 37 and in the second section of Table 7. The effect of the sodium dodecylsulfate on the rate of adsorption of the alkylbenzenesulfonate is observed in Table 7 to be greater than that of phenol. This is to be expected since the dodecyl-

sulfate molecule is considerably larger than the phenol molecule and no doubt occupies a much larger area on the carbon surface if the entire alkyl chain is adsorbed.

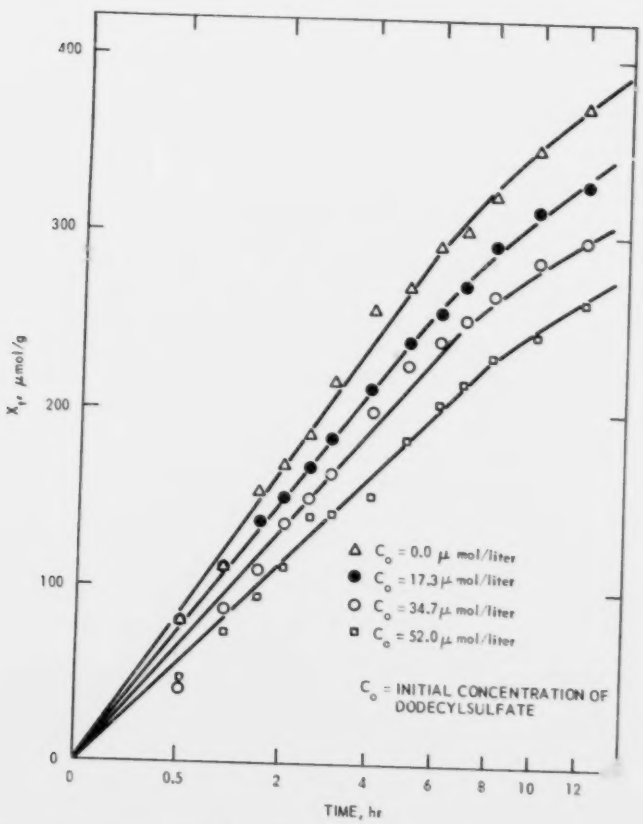

Figure 37. Effect of dodecylsulfate on rate of adsorption of (2-dodecyl)benzenesulfonate (30°C, 35.0 mg/liter, 0.126 mm Columbia Carbon).

While in both cases the presence of a second solute has been demonstrated to decrease the rate of adsorption of ABS, it can be seen from Table 7 that the sum of the rates of the two solutes is, in all cases where the two rates have been determined, much greater than the rate for ABS alone. This can be explained on the basis of the "diffusion pressure" or concentration effect discussed previously. The greater the total concentration of

molecules in the solution, the greater will be the "diffusion pressure" or concentration gradient.

The (2-dodecyl)benzenesulfonate obviously has a much greater effect on the rate of adsorption of the phenol than has the phenol on that of the surfactant. This indicates that, though the phenol molecule has a greater rate of diffusion in the pores of the carbon, an ABS molecule once having entered a pore may effectively block most of the cross-sectional area of that pore and thus retard the rate of diffusion of subsequent phenol molecules.

The relative effects of the two secondary solutes on the rate of adsorption of (2-dodecyl)benzenesulfonate as a function of concentration are shown in Figure 38. Note that the decrease in the rate for the primary solute is a linear function of the ratio of secondary to primary solute for the experimental range. This type of variation is characteristic of simple competition for adsorption sites.

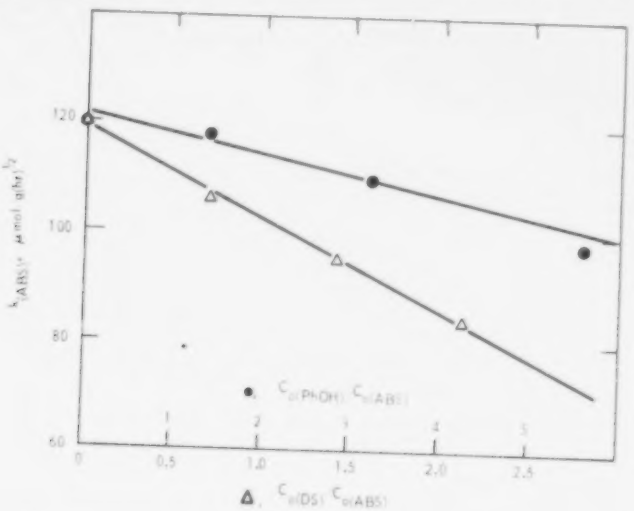

Figure 38. Effect of phenol and dodecysulfate on the rate of adsorption of (2-dodecyl)-benzenesulfonate (30°C, 35.0 mg. liter, 0.126 mm Columbia Carbon).

Capacities and Equilibria of Adsorption

Studies on the adsorption equilibria under competitive conditions were made with solutions containing phenol and (2-dodecyl)-benzenesulfonate. Determinations of the quantities of solutes adsorbed at equilibrium from these solutions indicated that the

equilibrium uptake of each solute on the activated carbon was affected adversely by the presence of the other. Indeed, it proved possible to describe the data quantitatively in terms of Langmuir-type equations for competitive adsorption.

By formal analogy to the equations developed by Langmuir for adsorption of individual species from mixtures of gases [12] and also to the expressions used for the description of competitive ion-exchange phenomena, [13] formulations for the competition between the phenol and ABS for adsorptive sites on the carbon were written. The expressions are:

$$X_A = \frac{X_{m,A}\ b_A\ C_A}{1 + b_A\ C_A + b_B\ C_B} \tag{6}$$

and

$$X_B = \frac{X_{m,B}\ b_B\ C_B}{1 + b_A\ C_A + b_B\ C_B} \tag{7}$$

where the symbols have the same significance as before and the subscripts A and B refer to the ABS and the phenol respectively.

When the concentrations of solutes are great enough so that surface coverage in the Langmuir sense is substantially complete, the quantity, unity, may be neglected in the denominators of Equations 6 and 7. These may then be linearized in the forms

$$\frac{C_A}{C_B} \cdot \frac{1}{X_A} = \frac{b_B}{b_A} \cdot \frac{1}{X_{m,A}} + \frac{C_A}{C_B} \cdot \frac{1}{X_{m,A}} \tag{8}$$

and

$$\frac{C_B}{C_A} \cdot \frac{1}{X_B} = \frac{b_A}{b_B} \cdot \frac{1}{X_{m,B}} + \frac{C_B}{C_A} \cdot \frac{1}{X_{m,B}} \tag{9}$$

If the Langmuir model described above applies to the experimental observations, plots of the quantities on the left-hand sides of Equations 8 and 9 as a function of C_A/C_B and C_B/C_A, respectively, should conform to straight lines that determine the magnitude of the indicated slopes and intercepts. Figure 39 illustrates this type of plot for the data from a series of equilibrium studies on adsorption from mixed solutions of phenol and (2-dodecyl)benzenesulfonate. Agreement with the expectations of the mathematical treatment is exhibited, each solute reducing the adsorption of the other in accordance with Equations 8 and 9.

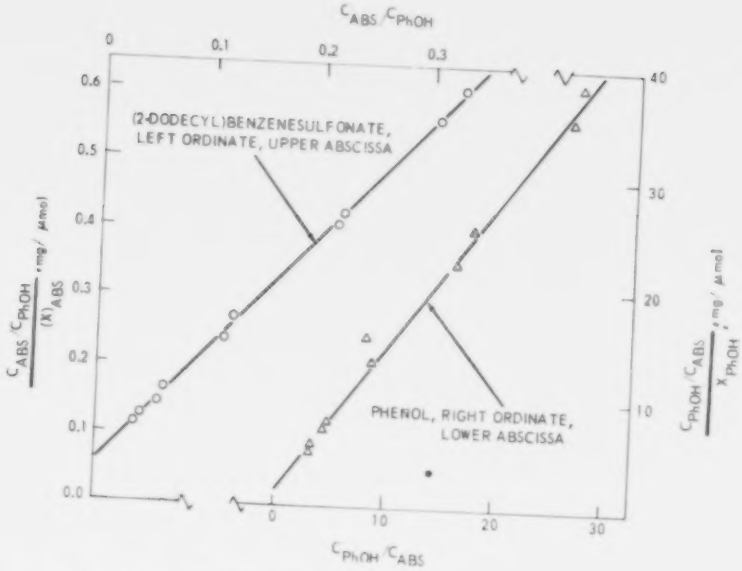

Figure 39. Competitive adsorption equilibria between phenol and (2-dodecyl)-benzenesulfonate (30°C, 32.0 mg/liter, 0.126 mm Columbia Carbon).

The magnitude of the competitive effect may be illustrated by noting that in a solution containing equal concentrations by weight of phenol and (2-dodecyl)benzenesulfonate the equilibrium adsorption of the phenol was 0.57 millimole per gram or a reduction of 25 percent compared with 0.75 millimole per gram from a pure solution of phenol at the same concentration. At the same time the amount of ABS adsorbed was 0.53 millimole per gram, or a reduction of 13 percent, compared with 0.61 millimole per gram for pure solution of the compound at the same concentration.

While the capacity of activated carbon for each solute in this bisolute system has been shown to be reduced relative to its value in pure solution, it is to be noted that the combined capacity of 1.10 millimole per gram was greater than that of either of the pure materials alone. It thus appears that total adsorptive capacities may be enhanced with mixed solutes. This observation, too, can be partially explained on the basis of the total increased concentration and hence the effect on adsorptive capacity, as in a single-solute system. Another explanation, perhaps even more appropriate than the former because data follow a Langmuir pattern that dictates an essentially constant value for X in the range of concentrations studied, is that the phenol and the ABS do not compete entirely for the same adsorption sites.

It is likely that the smaller phenol molecules can penetrate small pores that are not available to the ABS. The phenol molecules that can reach these pores are then not in competition with the ABS.

ADSORBENTS OTHER THAN ACTIVATED CARBON

Although activated carbon is the most widely used and presently the most effective adsorbent for treatment of aqueous solutions, there are two major problems associated with its use for the removal of pollutants from water and waste water. First is its high cost, which makes treatment of large volumes of contaminated water rather expensive unless the carbon can be economically regenerated. The second is the difficulty experienced in regenerating typical water-grade carbons because of their fragility.

A few preliminary experiments were conducted on possible alternative adsorbents, selected either for low cost and availability as waste materials or for prospective adaptability to regeneration.

Three materials were examined. Two of these, a fly ash obtained in the generation of gas from coal and a sludge ash from the wet incineration of sewage sludge, were waste materials that would be readily obtainable in many localities at practically no cost. Hence, if they proved to be effective adsorbents, they could be used once and discarded. The third was an activated aluminum oxide, the activation apparently having been achieved by controlled dehydration at about 500°C. Since complete oxidation of organic matter by air occurs fairly rapidly at 500°C, it seemed that this last material might be easily regenerable for re-use.

Figure 40 shows results of some preliminary adsorption experiments on these materials with solutions of (2-dodecyl)benzenesulfonate. The results with the two forms of ash indicate that these materials may be unsuitable as adsorbents for general treatment of waste waters, but further testing is necessary before any conclusions can be made. Capacities for adsorption were very low. The rapid attainment of a steady state by the sludge ash indicates that adsorption occurs only on the relatively small external surface. On the other hand, the somewhat increased adsorption with time for the fly ash points to a possibility of some porosity, but the capacity even after a long period of contact was still very low.

The results with the activated aluminum oxide were quite promising. The rate of adsorption was comparable with that for granular carbon of the same size. While the final uptake per

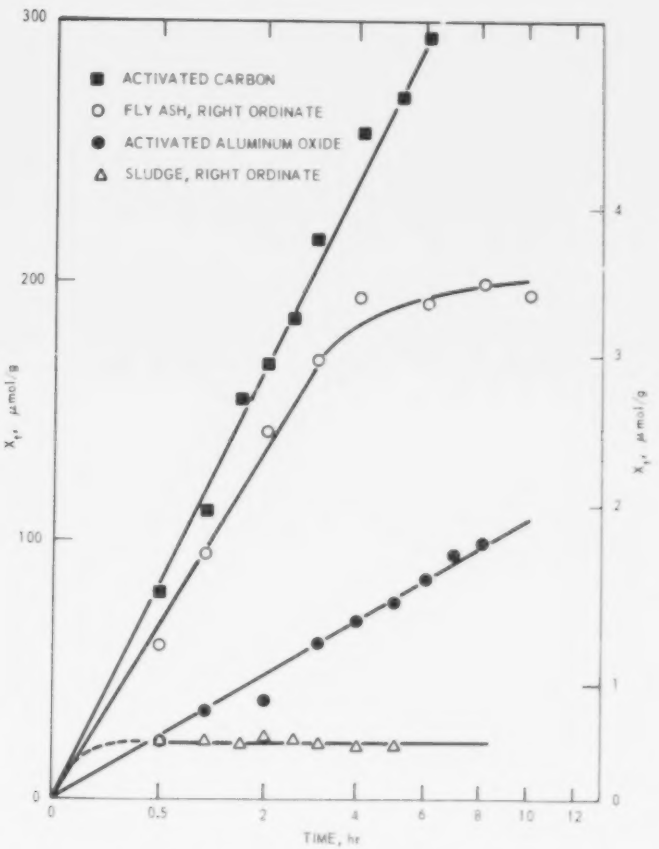

Figure 40. Rates of adsorption of (2-dodecyl)benzenesulfonate on selected adsorbents (30°C, 0.126 mm particle size).

gram was only about one-third that of Columbia Carbon, the capacity per milliliter of adsorbent was much more nearly equal because of the considerably greater density of the bauxite. If this material shows equally good adsorptive properties for other materials and if it proves to be readily regenerable without substantial attrition or disintegration, it could well be an excellent material for water renovation.

SUMMARY AND CONCLUSIONS

It has been observed that relatively rapid initial rates of adsorption of typical refractory materials on granular carbon decrease progressively and markedly to give rather slow approach to equilibrium conditions, which are attained completely only after several days of contact. This rate pattern is most readily explained by the hypothesis that rates of uptake by granular activated carbon are controlled by rates of diffusion of solute in the pores of the carbon, a phenomenon already well known for adsorption by other types of granular adsorbents as well as carbon. Theoretical treatments of intraparticle diffusion rates yield rather complex equations differing in form for different shapes of particle, but all have the characteristic that the preferred function of time for plotting purposes is $t^{1/2}$ rather than t; nearly linear variation of the amount adsorbed with $t^{1/2}$ has been found to obtain for the initial fractions of the adsorptive reactions studied.

The initial slopes, each termed k, obtained from plots of amounts of solute adsorbed versus $t^{1/2}$ have been used for comparison of relative rates of adsorption. Although the k values so obtained do not have the normal dimensions for rates and so cannot be called rate constants, relative values for appropriately similar conditions are useful rate parameters.

Relative rates of adsorption, as measured by values of k, have been found to vary reciprocally as the square of the radial diameter of the cylindrical particles used in the experiments. If the effect were simply a result of differences in specific external area, a reciprocal variation with the first power of the diameter would be expected. The variation observed is, however, in accord with theoretical equations for intraparticle diffusion.

Other data agreeing with the hypothesis that intraparticle diffusion is rate determining in adsorption by granular carbon are those for the temperature dependence of the rate of adsorption. Variations of diffusion rates of large molecules in water with temperature are usually found to conform to apparent activation energies of 3 to 5 kilogram-calories. An activation energy of 4.3 kilogram-calories has been computed from experimental data for the uptake of ABS by granular carbon, within the expected range for diffusion-controlled processes.

Over the range of experimentation, values of k have been observed to increase with increasing concentration of solute. Indeed, within this range, ratios of k to the square root of the initial concentration are constant. The observed relationship indicates that adsorption of detergent from water should be

relatively more rapid the more dilute the solution; that is, a greater fraction of solute should be adsorbed in a given period of time. This is advantageous for the cleanup of final traces of material in the renovation of a waste water.

A steady decline in rates of adsorption with increasing molecular weight of the solute has been noted in studies with phenol and a series of alkylbenzenesulfonates - an expected trend - for as molecular size increases, the rate of diffusion tends to become less. For adsorption from equimolar solutions, values of k ranged from 232 micromoles per gram - $(hour)^{1/2}$ for phenol and 220 for benzenesulfonate to 85 for (2-tetradecyl)benzenesulfonate.

The structure of the alkyl chain attached to the benzene ring in a molecule of ABS appears to exert a measurable influence on rate of adsorption. The k value for (2-dodecyl)benzenesulfonate, 118 micromoles per gram - $(hour)^{1/2}$, in which the linear side chain is attached to the benzene ring close to one end of the chain, is significantly greater than that for (6-dodecyl)benzenesulfonate, 96 micromoles per gram - $(hour)^{1/2}$, in which the attachment is near the center of the alkyl chain. The chain of the former compound is probably more able to coil to form a compact and thus more rapidly diffusing structure than is the bifurcated chain of the latter compound. This explanation also accounts for a smaller k value found for technical dodecylbenzenesulfonate, 50 micromoles per gram - $(hour)^{1/2}$. The pronounced branching of the great majority of the alkyl chains in the technical material would tend to inhibit flexibility and attainment of compactness.

Although rates of uptake of large-molecule compounds such as ABS by granular carbon are rather low, the ultimate capacity of the porous adsorbent for surfactants, after a sufficiently long period of contact, is quite large — about 15 percent by weight. Furthermore, quantities nearly this great are adsorbed from solutions of quite small concentrations of solute — about 3 micromoles per liter or 1 milligram per liter for dodecylbenzenesulfonate.

Detailed quantitative experiments have been conducted to evaluate total active surface areas by the conventional method based on adsorption from concentrated solutions of phenol, and to measure adsorption isotherms for solution concentrations ranging from 0.1 to 20 milligrams per liter for phenol and numerous alkylbenzenesulfonates. Evaluations of surface area have been used to compare the properties of the carbon employed in this research with other preparations of carbon described in the literature. Moreover, the surface area computed from

measurements with large concentrations of phenol has been compared with observed adsorption in the milligram-per-liter range to obtain estimates of the fraction of active surface being used.

By employing the Brunauer-Emmett-Teller equation for correlation of the isothermal equilibrium data at relatively large concentrations, the specific surface area of the carbon used in the research has been evaluated as 800 square meters per gram, an area that accords well with values reported for similar activated carbons.

Data for the lower concentration range — less than 60 micromoles per liter — have been correlated with the Langmuir equation. The value of the limiting adsorption of phenol found with the Langmuir equation corresponds to a specific active surface area of 270 square meters per gram, or approximately one-third the previous area.

Adsorption isotherms for alkylbenzenesulfonates at micromolar concentrations also conform to the Langmuir equation, but attainment of apparent saturation occurs at a much lower concentration for the long-chain alkylbenzenesulfonates than for phenol.

A somewhat surprising decrease in capacity from 1.09 millimoles per gram for phenol to 0.16 for benzenesulfonate has been observed. This difference in capacity for two molecules so similar in size may be the result of mutual repulsion by the charged sulfonate ions so that they are not able to pack nearly as closely on the surface as are molecules of phenol. The observed increase in capacity with increasing size of the alkyl group on the benzene ring of the ABS molecule may be a result of an insulating effect of the alkyl group that allows closer packing.

An identical capacity for adsorption by carbon, 0.40 millimoles per gram, has been observed for the three dodecylbenzenesulfonates studied. This value is only 40 percent of the capacity for phenol in micromolar solutions on a molar basis. The capacity for the dodecylbenzenesulfonates on a weight basis is, however, 140 milligrams per gram — significantly greater than the 103 milligrams per gram found for phenol.

That the experimental isotherm data represent true equilibrium conditions has been shown by desorption studies that show distributions of ABS between carbon and solution agreeing satisfactorily with those found in uptake experiments.

Experiments on adsorption from mixed solutions of ABS and phenol, and of ABS and sodium lauryl sulfate, have been conducted to gain some knowledge of the expected behavior of carbon in complex mixtures such as waste waters. In contrast with previous findings of others, each solute appears to compete in some way with the adsorption of the other.

The value of the rate parameter, k, for adsorption of phenol from approximately 30-micromolar solution has been found to be 220 micromoles per gram -(hour)$^{1/2}$ in the presence of a nearly equimolar concentration of ABS, a considerable decrease from the 310 micromoles per gram -(hour)$^{1/2}$ for adsorption from a pure solution of the same concentration. With equimolar concentrations of phenol and ABS the rate of adsorption of (2-dodecyl)benzenesulfonate is not measurably affected; with increasing proportions of phenol, however, the rate decreases steadily.

Additional studies with (2-dodecyl)benzenesulfonate and sodium lauryl sulfate as solutes have demonstrated that the latter material also adversely affects the rate of adsorption of ABS. Sodium lauryl sulfate competes a bit more actively with ABS than does phenol; the rate of adsorption of (2-dodecyl)benzenesulfonate is decreased to roughly 80 percent of its value for pure solution in the presence of approximately equimolar concentrations of sodium lauryl sulfate.

Measurements of the quantities of solute adsorbed at equilibrium from solutions containing both ABS and phenol have shown that the capacity of the carbon for each solute is affected adversely by the presence of the other. Indeed, it has been possible to describe the data quantitatively in terms of a Langmuir-type model for competitive adsorption. The observed data agree well with the formulations of the mathematical treatment, each solute reducing the adsorption of the other quantitatively in accord with expectations. In a solution containing equal concentrations by weight of phenol and (2-dodecyl)benzenesulfonate the equilibrium adsorption of the phenol is reduced by 25 percent from that for a solution of pure phenol at the same concentration, and the amount of ABS adsorbed is reduced by 13 percent from the value obtained for adsorption from an equal solution of the pure compound. It is significant, however, that the combined capacity is considerably greater than that for either of the pure solutes. It thus appears that a decrease of the adsorptive capacity of any individual solute occurs in solutions containing several compounds, but that the total adsorptive capacity of the adsorbent is enhanced in such systems.

Although granular carbon has been shown to be an excellent adsorbent with large capacity for many resistant organic pollutants in water, the slowness with which full capacity was attained in the batch experiments makes a consideration of techniques important for more effective utilization of the large capacity. The ensuing approximate computations indicate that suitable conditions can be realized in practice.

For full-scale application, columnar operation is envisaged, preferably continuous. Continuity of operation might be achieved by backflow operation with fresh carbon being fed to the top of the column and exhausted carbon being withdrawn from the bottom. The polluted water would flow countercurrently to this, entering at the bottom and overflowing at the top after renovation. The advantage of this form of operation is that it allows the use of small particles without excessive headloss through the bed.

Computations based on the use of carbon particles 0.1 millimeter in diameter indicate that an upward flow of 1 gallon per square foot per minute would expand such a bed by a factor of 2. On the assumption that the settled bed is 50 percent void space, the carbon content of the expanded bed would be about 25 percent, giving a weight of carbon in the column equal to about 12.5 pounds per cubic foot. If a 10-foot depth of expanded carbon were used, then the total carbon in the column would be 125 pounds per square foot of cross section.

In such a column the linear flow rate would be 0.19 foot per minute, giving a contact time for any portion of liquid equal to about 50 minutes. This time appears very short compared with the period of 10 days or so required to saturate the carbon in the batch experiments. Those experiments, however, were with very small amounts of carbon. With 25 percent carbon the time for removal of 50 milligrams of organic pollutants per liter on fresh carbon with a conservative k value of 50 micromoles per gram-(hour)$^{1/2}$ is about 1 minute or 0.2 foot of travel in the bed. Thus, effective removal of the organic material is to be expected.

The computation of particular relevance to utilization of the full capacity of the carbon is the length of time it can be used for adsorption before the column is exhausted. If 50 milligrams of organic matter per liter is to be removed, if the carbon capacity is taken as 0.1 gram per gram, and if the flow rate is 1 gallon per square foot per minute, then the carbon in a 10-foot column will last 500 hours, or about 20 days, before it is saturated. This time is ample to realize the full capacity.

At an estimated price of $400 per ton for the type of carbon used in these experiments and a requirement of 4,000 pounds of carbon for removal of 50 milligrams of organic matter per liter from 1 million gallons of polluted water, the cost of carbon, with the assumption of no regeneration, would be $800 per million gallons. In most instances the amount of organic pollutant to be removed would probably be less than 50 milligrams per liter and it should be possible to realize capacities greater than 0.1 gram per gram for the carbon, with corresponding reductions in cost.

Although this estimated cost is high compared with present costs of biological treatment, it is not completely out of line, and reactivation of the carbon should substantially reduce the overall costs.

APPENDIX A: NOTATIONS

A	Frequency factor in Arrhenius equation for variation of rate with temperature; constant in B.E.T. equation, expressive of energy of interaction with surface; subscript denoting reference to ABS.
A^o	Angstrom unit.
B	Subscript denoting reference to phenol.
b	Constant in Langmuir equation, expressive of energy of interaction with surface.
C_{eq}	Residual concentration in solution at equilibrium.
C_o	Initial concentration in solution.
C_s	Residual concentration in solution at saturation level of adsorbent.
C_t	Residual concentration in solution at time t.
^oC	Degree Centigrade.
E	Activation energy.
e	Base of natural logarithms.
H	Heat of adsorption.
k	Relative rate parameter.
M	Molecular weight.
$\underline{M}$	Molar concentration.
m	Concentration of adsorbent.
N	Avogadro's number.
o	Ortho.
p	Para.
R	Universal gas constant.
rpm	Revolutions per minute.

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r	Ratio of initial molar concentration of phenol to initial molar concentration of ABS.
T	Kelvin-scale temperature.
t	Time.
X	Amount of solute adsorbed per unit weight of adsorbent, (x/m).
X_{eq}	Value of X at equilibrium.
X_m	Value of X for complete monolayer coverage.
X_t	Value of X at time t.
x	Concentration of solute adsorbed from solution, $(C_o - C_t)$.
Δ	Incremental difference.
Σ	Specific surface area per unit of adsorbent.
σ^o	Molecular cross-sectional area of a molecule.

GPO 810—964—6

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GPO 810-864-7

(Continued from inside front cover.)

		Report Number
AWTR-7	Advanced Waste Treatment by Distillation	999-WP-9
AWTR-8	Ultimate Disposal of Advanced-Treatment Waste	999-WP-10
	Part 1. Injection	
	Part 2. Placement in Underground Cavities	
	Part 3. Spreading	
AWTR-9	Adsorption of Biochemically Resistant Materials from Solution. 1.	999-WP-11